

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

**Tetradentate amide extraction agents  
for trivalent lanthanides**

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CHALMERS UNIVERSITY OF TECHNOLOGY

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Cover:

The crystal structure of the cation of  $[\text{NdL}_2] \cdot (\text{ClO}_4)_3 \cdot \text{C}_2\text{H}_5\text{OH}$  (**18**), where L is the tetradentate amide **8**.

The atoms depicted: C (black), O (red), H (grey), N (blue), Nd (pink).

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# **Tetradentate amide extraction agents for trivalent lanthanides**

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## **Abstract**

Lanthanides are valuable materials. They are used in catalysts, permanent magnets, batteries, optical devices, and in many other products. Lanthanides are mainly supplied by mining industry, which generates large volumes of waste due to relatively low concentrations of these elements in geological deposits. Recovery of lanthanides from end-of-life items could contribute to the supply of these elements and thus decrease waste generation from mining.

Solvent extraction is the dominant method for separation of lanthanides on commercial scale. It can also be used in hydrometallurgical recovery of lanthanides from waste streams. One disadvantage of current extraction processes is the need to use a large number of separation stages and, accordingly, large amount of chemicals. The extractants with the enhanced affinity for lanthanides could remedy this problem.

In this work novel tetradentate amide extractants, designed and synthesized for extraction of lanthanides, are reported. The distribution ratios of lanthanides were found to be higher in the reactions with these amides than with the bidentate malonamides. This is due to a difference in the entropic effects, associated with the extraction of the metals by the malonamides and the new reagents. Solvent extraction, X-ray crystallography and mass spectroscopy have been used to investigate the interactions of f-block elements with the new extractants.

**Keywords:** lanthanides; malonamides; solvent extraction; single-crystal X-ray diffraction; electrospray ionization – mass spectrometry; entropic effect

## List of publications

This thesis is based on the work contained in the following papers:

### ***Paper I:***

Tyumentsev, M.S., Foreman, M.R.St.J., Ekberg, C., Matyskin, A.V., Retegan, T., Steenari, B.-M. The solvent extraction of rare earth elements from nitrate media with novel polyamides containing malonamide groups. *Hydrometallurgy* **2016**, 164, 24–30.

### ***Paper II:***

Tyumentsev, M.S., Foreman, M.R.St.J., Slawin, A.M.Z., Cordes, D.B., Savolainen, O., Ylmén, R., Steenari, B.-M., Ekberg, C. Coordination of trivalent lanthanides with bismalonamide ligands: implications for liquid-liquid extraction. *European Journal of Inorganic Chemistry*, **2017**, 4285–4298.

### ***Paper III:***

Tyumentsev, M.S., Foreman, M.R.St.J., Steenari, B.-M., Slawin, A.M.Z. Crystal structure and identification of resonance forms of diethyl 2-(3-oxoiso-1,3-dihydrobenzofuran-1-ylidene)malonate. *Acta Crystallographica Section E* **2017**, 73, 1576–1579.

### ***Paper IV:***

Tyumentsev, M.S., Foreman, M.R.St.J., Steenari, B.-M., Ekberg, C. Temperature effect on the distribution of lanthanide(III) ions in the perchlorate-malonamide-methyl isobutyl ketone systems. Accepted for publication in *The Journal of Chemical Thermodynamics*, **2018**. DOI: 10.1016/j.jct.2018.10.021.

### ***Paper V:***

Tyumentsev, M.S., Matyskin, A.V., Foreman, M.R.St.J., Steenari, B.-M., Ekberg, C. Extraction of f-block elements with the bismalonamides. *Manuscript*, **2018**.

### ***Contribution report:***

Main author of all the papers, experimental work and data processing with the exception of part of the single-crystal XRD analyses in papers II and III and the ESI-MS analyses in paper II.

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## 1. Introduction

Lanthanides are the fifteen f-block elements from lanthanum to lutetium. Together with yttrium (Y) and scandium (Sc) they form the group of rare earth elements (REEs) [1]. These elements are relatively abundant<sup>1</sup> in the Earth's crust [1] and may be concentrated in geological deposits, such as ion-adsorption clays [2]. Besides geological deposits, rare earth elements<sup>2</sup> can be found, in relatively large quantities, in the irradiated nuclear reactor fuels as one of the main fission products of uranium [3].

There is a large variety of applications for rare earth elements [4-6]. The U.S. geological survey (USGS) estimated distribution of rare earths by end use in the United States in 2017 as follows: catalysts, 55 %; ceramics and glass, 15 %; metallurgical applications and alloys, 10 %; polishing, 5 %; and other, 15 % [2]. In many applications the rare earths, due to their unique properties, cannot be substituted without a decrease in quality [2], which leads to high demand for REEs by various industries. Currently this demand is satisfied by mining.

In 2017 the world mine production of rare earth oxides was estimated to be 130 thousand tons [2].

Waste streams, such as industrial residues and REE-containing end-of-life products, are regarded as a potential source of rare earth elements, which could complement the supply of these elements from primary sources, i.e. geological deposits [5].

Rare earths are extracted from ores into aqueous solutions by digestion with mineral acids. Pure rare earth elements (individual or as a mixture) are normally obtained from the solutions by solvent extraction, which has been used for separation of these elements since the 1950-s [1, 7-10]. Today solvent extraction is the predominant method for separation of rare earth elements on commercial scale [1, 7]. The commercial extractants for rare earth elements are the carboxylic acids (e.g. Versatic<sup>®</sup> or naphthenic acids) and the organophosphorus acids (e.g. DEHPA) and esters (e.g. TBP)<sup>3</sup> [7]. The limited affinity of these monofunctional extractants for lanthanide(III) and actinide(III) ions in acidic media leading to a large number of separation stages and chemical use [7] was an incentive for development of polydentate extractants. It has been argued by many researchers [11-17], that, since trivalent lanthanide ions have high coordination numbers (CN) in solutions (CN = 6 – 12) [1], polydentate solvent extraction ligands may extract lanthanides(III) with higher distribution ratios than the commercial extractants due to the entropic effect.

## 2. Objectives

The goal of this work was to design and synthesize new selective polydentate amide ligands, evaluate their capability of extracting lanthanides(III) from aqueous solutions and compare with already existing amides and other commercial extractants. The derivatives of malonamides were selected for this purpose due to their stability against hydrolysis, affinity for lanthanide(III) ions and adherence to the 'CHON' principle<sup>4</sup>. Different investigations were carried out to accomplish this complex goal: synthesis of a series of amides, stoichiometric studies and complex formation studies in solid and liquid states.

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<sup>1</sup> Even lutetium (80 ppb), being the rarest lanthanide, is more abundant in the Earth's crust than silver (70 ppb), bismuth (9 ppb), gold (4.3 ppb) and tellurium (1 ppb) (Vinogradov, 1962). 1 ppb =  $1 \cdot 10^{-4}$  wt. %.

<sup>2</sup> Both radioactive and stable isotopes.

<sup>3</sup> DEHPA is di-(2-ethylhexyl)phosphoric acid. TBP is tri-*n*-butyl phosphate.

<sup>4</sup> The 'CHON' principle is the criterion for a solvent extraction ligand, used in an advanced spent nuclear fuel reprocessing, to be composed of carbon, hydrogen, oxygen and nitrogen atoms only. The ligands, complying with the principle, are completely incinerable and thus do not generate incombustible secondary waste.

### 3. Theory

#### 3.1 Coordination of lanthanides

Lanthanides form coordination complexes, in which a single central metal ion is surrounded by several ligands. Lanthanides exhibit specific features in their coordination complexes [1]:

1. A broad range of coordination numbers (generally 6 – 12);
2. Coordination geometry is determined by ligand steric factors rather than crystal field effects;
3. Lanthanides form labile ‘ionic’ complexes;
4. The 4f orbitals in a lanthanide(III) ion do not participate directly in bonding, being well shielded by the 5s<sup>2</sup> and 5p<sup>6</sup> orbitals. The spectroscopic and magnetic properties of lanthanides are thus largely uninfluenced by a ligand;
5. Lanthanides prefer anionic ligands with donor atoms of high electronegativity (e.g. O, F);
6. Lanthanides readily form hydrated complexes, which can cause uncertainty in assigning coordination numbers;
7. The oxidation state of lanthanides in aqueous solution is predominantly (3+);
8. Lanthanides do not form multiple bonds with oxygen or nitrogen atoms;
9. There is a decrease in radius of a lanthanide(III) ion on crossing the series from La to Lu, which is referred to as the lanthanide contraction;
10. In some cases it is possible to group complexes of lanthanides into four tetrads, when the logarithm of a certain parameter of a complex (e.g. distribution ratio) is plotted against the atomic numbers of lanthanides.

The stoichiometry of coordination complexes of lanthanides can be assessed by several experimental techniques such as solvent extraction and mass spectrometry (for liquid state complexes), and single crystal X-ray diffraction (for solid state complexes).

##### 3.1.1 Determination of stoichiometry of lanthanide complexes formed during solvent extraction

Solvent extraction is the distribution of a solute between two immiscible liquid phases in contact with each other, i.e. a two-phase distribution of a solute [7]. This distribution is characterized by distribution ratio, which is defined as the ratio between total analytical concentrations of the species in organic and aqueous phases, denoted as  $C_{(org)}$  and  $C_{(aq)}$ , respectively at equilibrium [7]:

$$D = C_{(org)}/C_{(aq)}, \quad (1)$$

In this work, the concentration of a distributed species in the organic phase  $C_{(org)}$  has been calculated from the difference between the initial  $C_0$  and the equilibrium aqueous phase  $C_{(aq)}$  concentrations of the species, i.e. through a material balance for the extraction system:

$$C_{org} = (C_0 - C_{(aq)})/\theta, \quad (2)$$

where  $\theta$  is the ratio between volumes of an organic  $V_{(org)}$  and an aqueous  $V_{(aq)}$  phases:

$$\theta = V_{(org)}/V_{(aq)}. \quad (3)$$

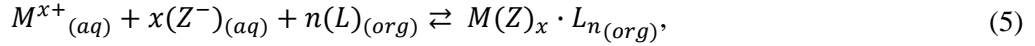
If distribution ratios are calculated from two independent measured quantities  $C_0$  and  $C_{(aq)}$ , assuming volume phase ratios ( $\theta$ ) to be constant, the standard uncertainties of distribution ratios ( $\sigma_D$ ) can be calculated using the formula for a propagation of random errors [18]:



$$\sigma D = \left( \frac{C_0}{C_{(aq)}} \right) \times \sqrt{\left( \frac{\sigma C_0}{C_0} \right)^2 + \left( \frac{\sigma C_{(aq)}}{C_{(aq)}} \right)^2}, \quad (4)$$

where  $\sigma C_0$  and  $\sigma C_{(aq)}$  are the standard uncertainties of the concentrations  $C_0$  and  $C_{(aq)}$ , respectively.

Amides, e.g. malonamides [19], are Lewis bases. Therefore they might be able to coordinate with Lewis acids such as  $H^+$  and lanthanide(III) ions. These reactions can be described by the equilibrium equation:



where  $M^{x+}$  denotes  $H^+$  ( $x = 1$ ) or  $Ln^{3+}$  ( $x = 3$ ) ions;  $Z^-$  denotes single charged anions  $NO_3^-$  or  $ClO_4^-$ , used in this work;  $L$  stands for a molecule of an amide;  $M(Z)_x \cdot L_n$  is an extracted species (an adduct);  $x$  and  $n$  are the stoichiometric coefficients; the subscripts  $(aq)$  and  $(org)$  refer to aqueous and organic phases, respectively.

When using the eqn. (5) to describe extraction reactions of either  $H^+$  or lanthanides(III) with an amide, it is assumed that the extraction mechanism is the adduct formation [7]. Thus the extraction reaction (eqn. 5) can be describe by the equilibrium constant  $K_{ex}$ :

$$K_{ex} = \frac{\{M(Z)_x \cdot L_n\}_{(org)}}{\{M^{x+}\}_{(aq)} \times \{Z^-\}_{(aq)}^x \times \{L\}_{(org)}^n}, \quad (6)$$

where braces indicate chemical activities of the species in the aqueous  $(aq)$  and organic  $(org)$  phases at equilibrium.

In this work the apparent equilibrium constants of extraction reactions were used. They were obtained from eqn. (6) by replacing the chemical activities of the species by their analytical concentrations. These apparent equilibrium constants are valid for the specific experimental conditions. This is however not a limitation since these constants are used mainly for the determination of the stoichiometric coefficients at the current experimental conditions. Further in the text square brackets are used to indicate analytical concentrations of the species in the aqueous  $(aq)$  and organic  $(org)$  phases at equilibrium.

The distribution ratio ( $D_M$ ) of a cation  $M^{x+}$  is described by the equation:

$$D_M = \frac{[M(Z)_x \cdot L_n]_{(org)}}{[M^{x+}]_{(aq)} \times (1 + \sum_{i=1}^p \beta_i \times [Z^-]_{(aq)}^i)}, \quad (7)$$

where  $\beta_i$  is an cumulative stability constant [20] of a complex  $[M(Z)_i]_{(aq)}^{(x-i)}$  in an aqueous phase,  $p$  is the maximum number of complexes of  $M^{x+}$  with anion  $Z^-$ , which can be formed in an aqueous phase.

The combination of eqns. (6) and (7) gives the equation (8):

$$\log \left( \frac{D_M}{[Z^-]_{(aq)}^x} \right) = \log \left( \frac{K_{ex}}{1 + \sum_{i=1}^p \beta_i \times [Z^-]_{(aq)}^i} \right) + n \times \log [L]_{(org)}. \quad (8)$$

According to the equation (8) the dependence of  $\log(D_M/[Z^-]_{(aq)}^x)$  on  $\log [L]_{(org)}$  is the linear function with the slope ( $n$ ), provided the total concentration of  $Z^-$  ions in the aqueous phase does not change upon the extraction of  $M^{x+}$ .

The slope ( $n$ ) is the empirical stoichiometric coefficient of the extraction reaction. It indicates the number of extractant molecules per one  $M^{x+}$  cation in the extracted species.

In the reactions of nitric acid extraction  $p = 1$  (eqn. 8). Trivalent lanthanides can form several nitrate complexes, in which the number of the coordinating nitrates ranges from one to six [1, 20, 21]. However

only two nitrato complexes of lanthanides(III)  $[\text{LnNO}_3]^{2+}$  and  $[\text{Ln}(\text{NO}_3)_2]^+$  are usually considered to be dominating in the aqueous nitrate media with moderate total nitrate concentration [22].

The perchlorate ions are weakly coordinating [23]. Therefore the reactions of lanthanide(III) extraction from perchlorate media can be described by the simplified equation:

$$\log D_{Ln} = \log K_{ex} + 3 \times \log [\text{ClO}_4^-]_{(aq)} + n \times \log [L]_{(org)}, \quad (9)$$

where  $L$  is a molecule of extractant,  $n$  is the stoichiometric coefficient.

### 3.1.2 Determination of stoichiometry and geometry of lanthanide complexes by X-ray diffraction

When it is possible to grow single crystals of lanthanide complexes, X-ray diffraction can be used to determine its stoichiometry and geometry, i.e. precise shapes, bond distances, and angles. This technique relies on the fact that the atomic spacing in crystals is of the same magnitude as the wavelength of X-rays diffraction grating to a beam of X-rays.

Ligands used for solvent extraction of metal ions usually contain long alkyl groups in their structures to enhance the solubility of the extracted complexes in organic solvents. As a rule, such ligands are not suitable for collecting crystallography data because long alkyl groups decrease the crystallinity of metal complexes.

Homologous ligands with shorter alkyl groups have to be used instead for growing crystals, since it is argued that they form complexes with an equal coordination environment of a metal e.g. [24]. For instance, the alkyl groups of different length in the  $N,N,N',N'$ -tetraalkylsubstituted malonamides: methylmalonamide [25], ethylmalonamide [26] and butylmalonamide [27] do not change the coordination environment of a lanthanum(III) central ion in the respective nitrato crystal complexes in terms of the number of the coordinating ligands and their coordination modes.

## 3.2 Synthesis of amides

In this work the amides were synthesized for solvent extraction and crystal growth experiments. There are several routes, which can be used for synthesis of amides [28-31]:

1. The reactions of amines with: acyl chlorides, acid anhydrides, acid esters;
2. The reactions of dimethylcarbamoyl chlorides with carboxylates;
3. The reactions of carboxylic acids with alkylphosphoramides;
4. The reactions between a carboxylic acid and a secondary amine in the presence of a carbodiimide.

Commonly, amides are produced by reactions of amidation of amines (route 1). The reactivity of the amidating reagents in these reactions increases in the order: acid esters < acid anhydrides < acyl chlorides [28]. Acyl chlorides and acid anhydrides are more reactive but also generally more expensive than acid esters.

## 3.3 Thermodynamics of extraction

The values of the apparent equilibrium constants ( $K_{ex}$ ) of the lanthanide(III) extraction reactions were used to calculate the standard Gibbs energy changes  $\Delta_r G^\circ$  of the extraction reactions according to the equation:

$$\Delta_r G^\circ = -R \times T \times \ln K_{ex}, \quad (10)$$

where  $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is the molar gas constant,  $T$  is the absolute temperature of a reaction. The dependence of an equilibrium constant of a metal ion extraction reaction on temperature can be described by the van't Hoff equation [32]:

$$\ln K_{ex} = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{R \times T}, \quad (11)$$

where  $K_{ex}$  is the apparent equilibrium constant of an extraction reaction,  $\Delta_r S^\circ$  is a standard entropy change of a reaction,  $\Delta_r H^\circ$  is a standard enthalpy change of a reaction,  $R$  is the molar gas constant,  $T$  is the absolute temperature of a reaction.

According to the eqn. (11) the plot of  $\ln K_{ex}$  against  $1/T$  to a first approximation is the straight line with the gradient  $(-\Delta_r H^\circ/R)$  and the intercept  $(\Delta_r S^\circ/R)$ , if  $\Delta_r S^\circ$  and  $\Delta_r H^\circ$  are temperature independent. However in general standard entropy and enthalpy changes of extraction reactions may depend on temperature according to the following equations [32]:

$$\Delta_r H^\circ_{T_2} = \Delta_r H^\circ_{T_1} + \Delta C_p^\circ \times (T_2 - T_1), \quad (12)$$

$$\Delta_r S^\circ_{T_2} = \Delta_r S^\circ_{T_1} + \Delta C_p^\circ \times \ln(T_2/T_1), \quad (13)$$

where  $\Delta_r H^\circ_{T_1}$  and  $\Delta_r H^\circ_{T_2}$  are the standard enthalpy changes of a reaction at temperatures  $T_1$  and  $T_2$ , respectively;  $\Delta C_p^\circ$  is the difference in the standard molar heat capacity of reactants and products in the reaction at constant pressure;  $\Delta_r S^\circ_{T_1}$  and  $\Delta_r S^\circ_{T_2}$  are the standard entropy changes of a reaction at temperatures  $T_1$  and  $T_2$ , respectively. For small temperature intervals the change in a heat capacity is also small. Therefore, one can consider  $\Delta C_p^\circ$  as the temperature independent parameter for a narrow temperature range.

The standard Gibbs energy change of a reaction ( $\Delta_r G^\circ_T$ ) at absolute temperature  $T$  can be expressed as:

$$\Delta_r G^\circ_T = \Delta_r H^\circ_T - T \times \Delta_r S^\circ_T, \quad (14)$$

By the combination of eqn. (10) and eqn. (12) – (14) the modified van't Hoff equation can be obtained [33]:

$$\ln K_T = [-\Delta_r H^\circ_{T_0} \times T^{-1} - \Delta C_p^\circ \times (T - T_0) \times T^{-1} + \Delta_r S^\circ_{T_0} + \Delta C_p^\circ \times \ln(T/T_0)] \times R^{-1}, \quad (15)$$

where  $T_0$  is the absolute temperature, selected as the standard state;  $\Delta_r H^\circ_{T_0}$  and  $\Delta_r S^\circ_{T_0}$  are the standard enthalpy and entropy changes of a reaction at  $T = T_0$ ;  $K_T$  is an apparent equilibrium constant of an extraction reaction at absolute temperature  $T$ .

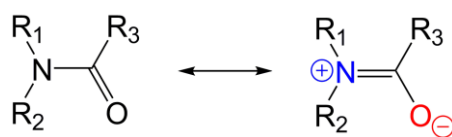
The eqn. (15) expresses  $\ln K_T$  as the function of temperature. The three fitted coefficients  $\Delta_r H^\circ_{T_0}$ ,  $\Delta_r S^\circ_{T_0}$  and  $\Delta C_p^\circ$  can be obtained from eqn. (15) if the values of  $\ln K_T$  are known for at least three temperatures. The standard state is the arbitrary parameter of eqn. (15), having the mathematical meaning [34].

## 4. Overview and assessment of amide extractants

Amides have been studied since the beginning of modern organic chemistry. However, studies concerning the utilization of amides as an alternative to tri-*n*-butyl phosphate in the reprocessing of irradiated nuclear fuel started in the early 1960-s [29]. The obtained results were promising and initiated the studies of amides as extractants for various metal ions including lanthanides. Chemical properties of amides have been finely tuned along the years, and the progress in this research area is briefly presented in this section.

### 4.1 Amides as extractants for trivalent lanthanides

Due to a resonance hybridization of the amide bond (Fig. 1) a carbonyl oxygen atom of carboxylic acid amides has high electron density [35].



**Figure 1** – Structures of standard (left) and charge separated (right) resonance <sup>5</sup> forms of *N,N*-disubstituted amide of a carboxylic acid  $R_3COOH$ .  $R_1$ ,  $R_2$ ,  $R_3$  – alkyl, aryl or H substituents.

The electron donor properties of this oxygen atom allow the amides to coordinate with Lewis acids <sup>6</sup> such as trivalent lanthanides [31]. In general tertiary amides (i.e. those with  $R_1 \neq H$  and  $R_2 \neq H$ ) are more basic than common solvating extractants such as tri-*n*-butyl phosphate (TBP) [31]. Some amides i.e. *N,N'*-dimethyl-*N,N'*-dibutylmalonamide (DMDBMA) are even more basic than tri-*n*-octylphosphine oxide (TOPO) [31]. Therefore, they bind Lewis acids stronger. Other advantages of carboxylic acid amides as metal extracting reagents over organophosphorus solvating extractants (e.g. TBP) are their enhanced hydrolytic stability and the radiolysis degradation products, which can be easily removed from the extraction systems [29]. Since amides are totally incinerable their use in nuclear fuel reprocessing could minimize generation of secondary wastes [36]. Besides most of the amides are prepared in only one or two steps in high yields (often up to 90 % or higher), and many of them can be conveniently purified by distillation [29, 31].

The vast majority of the amides, which have ever been used in solvent extraction of metal ions, contain either one (monoamides) or two (diamides) amide groups in their molecules, being amides of mono- and dicarboxylic acids respectively. The amide extractants with three and more amide groups (polyamides) are unusual [11, 37-40].

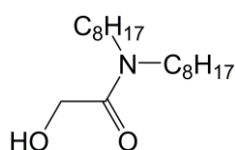
*N,N*-dialkyl substituted monoamides such as *N,N*-dimethylformamide or *N,N*-dimethylacetamide form O-bound crystal complexes with trivalent lanthanide ions [41]. However *N,N*-dialkylamides are very poor extractants for trivalent f-block elements in nitrate media [29, 42, 43]. For example, in the reactions with a 1 mole per liter solution of either *N,N*-di-*n*-butyl(2-ethyl)hexanamide (DBEHA) or *N,N*-di-*n*-hexyloctanamide (DHOA) in mesitylene at various nitric acid concentrations the measured distribution ratios of americium and europium were [44]:  $D_{Am(III)} < 10^{-1}$  and  $D_{Eu(III)} < 10^{-3}$ . Such low distribution

<sup>5</sup> The term ‘mesomerism’ (synonymous with ‘resonance’) is particularly associated with the picture of  $\pi$ -electrons as less localized in an actual molecule than in a Lewis formula. PAC, 1994, 66, 1077 (Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)). P. 1139.

<sup>6</sup> Lewis acids are acceptors of electron pair(s).

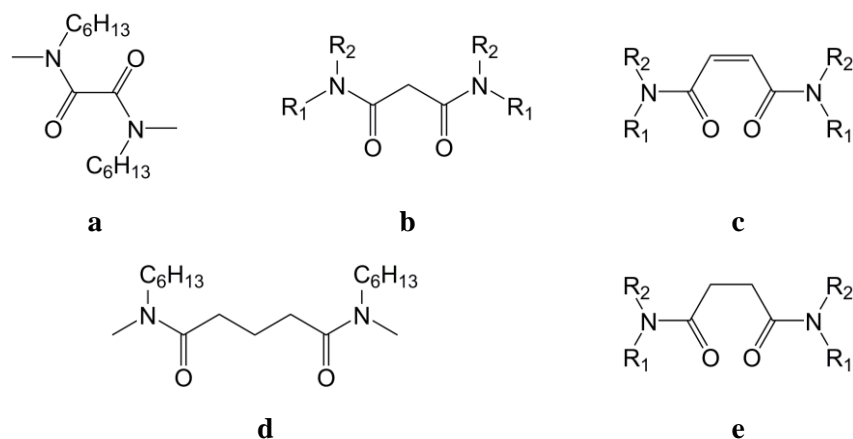
ratios do not permit the use of *N,N*-dialkylamides as extractants for the separation of trivalent f-block elements [29].

Most of monoamides are monofunctional extracting ligands. Monofunctional ligands are generally less strong extractants than their bifunctional analogues [45], which form strong chelate complexes [20] with metal ions. Therefore, distribution ratios of trivalent f-block elements can be expected to be higher in the reactions with bifunctional amides than with the monoamides. In agreement with these expectations the use of the bifunctional monoamide 2-hydroxy-*N,N*-dioctylacetamide (Fig. 2), which has one amide and one hydroxyl functional groups and forms chelate complexes with lanthanides(III), allowed to achieve higher distribution ratios of Am(III) and Eu(III) in dodecane than those values reported for the reactions with any other monoamide and malonamide, which has been argued by Kannan *et al.* [46].



**Figure 2** – Molecular structure of 2-hydroxy-*N,N*-dioctylacetamide.

The most common and well-studied (since the 1960-s [47]) bifunctional amide extractants are the diamides, having two amide functional groups in their molecules. The extraction properties of the diamides depend on their structures. Sasaki *et al.* studied the influence of the size of the linkage separating two amide groups in the homologous diamides (Fig. 3) on distribution ratios of actinides(III), (IV), (V), (VI) and lanthanides(III) [48]. It was established that the order of the extractability of diamides for Am(III) is the following [48]: **b** > **c** > **e** > **d** > **a** (aqueous phase – perchloric acid solution; diluent – nitrobenzene) (Fig. 3). The order for lanthanides Ln(III) was found to be: **b** > **e** > **c** (aqueous phase – nitric acid solution; diluent – *n*-dodecane) (Fig. 3) [48].



**Figure 3** – Molecular structures of the diamides: **a** – oxalamide, **b** – malonamide, **c** – maleamide, **d** – glutaramide, **e** – succinamide.  $R_1 = \text{CH}_3$ ,  $R_2 = \text{C}_6\text{H}_{13}$  for Am(III) extraction;  $R_1 = R_2 = \text{C}_8\text{H}_{17}$  for Ln(III) extraction [48].

Thus it was demonstrated [48] that: a) the malonamides are the best ligands for solvent extraction of trivalent f-block metals among all studied diamides; b) the shorter the linkage between two amide groups in a diamide molecule the higher the corresponding distribution ratios of Am(III) and Ln(III). The oxalamide (Fig. 3 **a**) having the shortest linkage between two amide groups among all studied diamides, namely the direct bond between two carbonyl atoms, is the exception from this rule. This diamide

extracts metal ions poorly likely due to a strong intramolecular electrostatic repulsion of carbonyl oxygen atoms discouraging a formation of chelate complexes with metals as suggested by Siddall *et al.* [47].

The diamides other than malonamides are considered to be good extractants for hexa- and tetravalent actinides (e.g. succinamides [49], glutaramides [50], adipamides [51]). However these are poor extractants for trivalent f-block elements [48, 52], despite some of them are able to form chelates with lanthanides(III) in solid-state nitrate complexes, e.g. *N,N,N',N'*-tetramethylsuccinamide [53]. For instance Charbonnel *et al.* reported that *N,N,N',N'*-tetrabutylglutaramide (a structural analogue of **d** from Fig. 3) extracts americium and europium from nitric acid solutions into toluene with low distribution ratios [50]:  $D_{Am(III)} \approx D_{Eu(III)} < 10^{-2}$ . Rao *et al.* established that *N,N,N',N'*-tetramethylmalonamide (TMMA) forms stronger complexes with Eu(III) perchlorate than *N,N,N',N'*-tetramethylsuccinamide in the acetonitrile – DMSO mixed solvent [54], which may explain the differences in the extraction properties of malonamides and other diamides.

## 4.2 Malonamides as extractants for trivalent lanthanides

The considerable interest of researchers for malonamides resulted from the ability of these ligands to extract trivalent f-block elements from aqueous solutions with high nitric acid concentrations [45].

### 4.2.1 Effects of structure of malonamides on extraction of lanthanides(III)

Malonamides are the diamide derivatives of malonic acid. The generic structure of a malonamide molecule is represented in Fig.4.



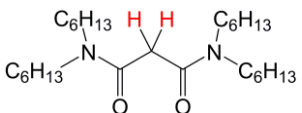
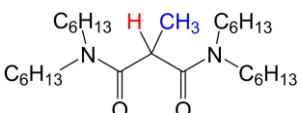
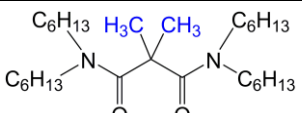
**Figure 4** – The generic structure of a malonamide molecule.  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  – substituents.

It was noticed by many researchers [28, 55-57] that the extraction properties of malonamides are strongly affected by the substituents:  $R_1$  and  $R_2$  at nitrogen atoms of amide groups and  $R_3$  at the bridging carbon atom connecting amide groups (Fig.4). The malonamides with alkyl, aryl or mixed  $R_1$  and  $R_2$  groups of different sizes were studied for extraction of trivalent lanthanides [28, 31, 55, 56, 58, 59]. Bulky (e.g. cyclohexyl, benzyl) or long alkyl-chain  $R_1$  and  $R_2$  substituents at the amide nitrogen atoms in malonamides decrease the distribution ratios of lanthanides(III), while the combination of short- ( $R_1 = CH_3, C_2H_5$ ) and long- ( $R_2 = C_6H_{13}, C_8H_{17}$ ) alkyl-chain groups provides the highest distribution ratios of trivalent f-block metals [28, 56]. Musikas *et al.* concluded that short alkyl-chain groups  $R_1$  limit the steric hindrance for metal coordination while long alkyl-chain groups  $R_2$  give necessary lipophilic character to a malonamide extractant [56]. Rao *et al.* showed that in acetonitrile solutions the malonamides with either  $R_1$  or both  $R_1$  and  $R_2$  bulky groups (i.e. butyl, isopropyl, hexyl) form weaker complexes with Eu(III) perchlorate than *N,N,N',N'*-methylmalonamide (TMMA) [60].

McNamara *et al.* conducted a systematic determination of the effects of alkyl substitution of the bridging (methylene) carbon atom ( $R_3$  and  $R_4$  substituents, Table 1) for a series of malonamides: *N,N,N',N'*-tetrahexylmalonamide (THMA), *N,N,N',N'*-tetrahexyl-2-methylmalonamide (MTHMA) and *N,N,N',N'*-tetrahexyl-2,2-dimethylmalonamide (DMTHMA) [61]. Methylation on the bridging carbon atom of THMA reduces the distribution ratio of europium(III) by nearly one order of magnitude (Table

1), and additional methylation on this atom in DMTHMA inhibits extraction of Eu(III) almost completely [61].

**Table 1** – Distribution ratios of Eu(III) in the reactions with the series of the malonamides. Aqueous phase: 3 M NaNO<sub>3</sub>, 1.5 mM HNO<sub>3</sub>. Organic phase: 0.5 M malonamide in *tert*-butylbenzene. Data is taken from [61].

Malonamide abbreviation	Malonamide structure	Bridging carbon substituents R <sub>3</sub> and R <sub>4</sub>	D <sub>Eu(III)</sub>
THMA		-H, -H	~ 1.5 · 10 <sup>-2</sup>
MTHMA		-H, -CH <sub>3</sub>	~ 1.5 · 10 <sup>-3</sup>
DMTHMA		-CH <sub>3</sub> , -CH <sub>3</sub>	< 10 <sup>-5</sup>

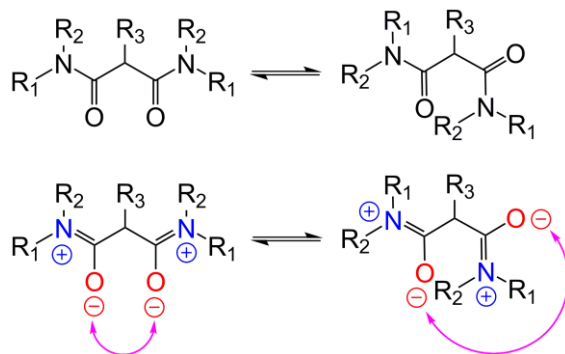
A steric crowding in the extracted complexes was suggested for an explanation of the decreased distribution ratios of Eu(III) upon alkylation of the bridging carbon [61]. It is worth to mention that for the only exception of DMTHMA no other malonamides with *bis*-substituted bridging carbons, i.e. those with R<sub>3</sub> ≠ H and R<sub>4</sub> ≠ H (Fig. 4), which would have been used as an extractant for metal ions, were found in the literature. In other words one of the substituents at the bridging carbon atom in molecules of all studied malonamide extractants other than DMTHMA is always a hydrogen atom, i.e. R<sub>4</sub> = H.

Rao *et al.* studied the complexation of Eu(III) perchlorate with THMA, MTHMA and DMTHMA in acetonitrile containing small amounts of DMSO [60]. It was found that the formation constants decrease in the order: MTHMA > THMA > DMTHMA, and no complexation of Eu(III) with DMTHMA was observed by using calorimetry and FT-IR [60].

While monoalkylation of the bridging carbon atom in THMA with short methyl group (R<sub>3</sub> = CH<sub>3</sub>) led to the decreased distribution ratios of Eu(III) [61], malonamides with long alkyl (R<sub>3</sub> = C<sub>6</sub>H<sub>13</sub> [55]) or alkyl-alkoxy (R<sub>3</sub> = C<sub>2</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>13</sub> [45, 55] or C<sub>2</sub>H<sub>4</sub>OC<sub>2</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>13</sub> [45]) substituent at the bridging carbon extract trivalent f-block elements with higher distribution ratios than the corresponding malonamides with R<sub>3</sub> = H at medium and high acidities of an aqueous phase ([HNO<sub>3</sub>] > 2 M). Nigond *et al.* showed for the series of R<sub>3</sub>-alkyl substituted *N,N'*-dimethyl-*N,N'*-dibutylmalonamides (R<sub>3</sub> = C<sub>14</sub>H<sub>29</sub>, C<sub>16</sub>H<sub>33</sub> and C<sub>18</sub>H<sub>37</sub>) that the solubility of the Nd(III) extracted species in an organic phase is increasing with the length of the R<sub>3</sub>-alkyl substituents [62], i.e. long R<sub>3</sub>-aliphatic groups enhance the lipophilicity of extracted metal complexes. An attempt was taken to improve lipophilicity of malonamides by replacing the R<sub>3</sub>-aliphatic substituent to the fluorinated one [63].

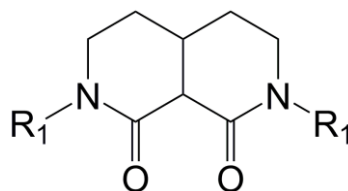
Spjuth *et al.* studied the effects of substituents R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> on basicity of malonamides and compared malonamides, possessing different basicities, in the reactions of Eu(III) and Am(III) extraction into *tert*-butylbenzene [19]. The highest distribution ratios of these metal ions were observed in the reaction with the malonamides having the lowest values of basicity [19]. These results are opposite to a typical extraction behavior of other solvating ligands [7].

It has been argued by Lumetta *et al.* that an important factor influencing the stability of chelate complexes of malonamides with trivalent lanthanide ions is the considerable strain induced in these chelates upon complexation [64]. The amide carbonyls in malonamides tend to align away from one another (Fig. 5, a right hand side of the equilibria) in order to balance the dipole moment of the molecule [64] for instance in the crystal structures of *N,N'*-diethyl-*N,N'*-dicyclohexylmalonamide and *N,N'*-diisopropyl-*N,N'*-dicyclohexylmalonamide (however with the exception of the *N,N'*-dimethyl-*N,N'*-diphenylmalonamide crystal structure probably due to  $\pi$ - $\pi$  stacking effects) [58].



**Figure 5**– The equilibria of malonamide conformers. The structures are depicted in standard (top) and charge separated (bottom) resonance forms. The curly arrows represent a distance between two negatively charged oxygen atoms repulsing each other.  $R_1$ ,  $R_2$ ,  $R_3$  – substituents.

This conformation of a free malonamide ligand is unfavorable for the chelate coordination to a metal ion [25]. The malonamides adopt a left hand side conformation, shown in Fig. 5, in all but one [65] studied crystal complexes with trivalent lanthanides [25, 26, 58, 66-68]. It was demonstrated that the strain effect is significantly reduced in the bicyclic malonamides (Fig. 6) due to a rigid framework of these molecules provided by the (*N,N'*, $R_3$ )-substituent [69].



**Figure 6** – A molecular structure of a bicyclic malonamide [25, 64, 69-71].  $R_1$  – aliphatic substituent.

Results from spectroscopic titrations indicate that the bicyclic malonamides exhibit a (10 – 100) fold increase in binding affinity to trivalent lanthanides over the acyclic malonamide [25]. As determined by solvent extraction in *tert*-butyl benzene, the affinity (i.e. the observed extraction constant) of the bicyclic malonamide (Fig. 6,  $R_1 = C_8H_{17}$ ) for Eu(III) is in the order of ten million times greater than that of the previously investigated malonamides including DMDBDTMA and DMDOHEMA [69].

Unfortunately the bicyclic malonamides have a disadvantage of forming a third liquid phase when their organic phase solutions are in contact with even weak nitric acid (0.5 M  $HNO_3$ ) [69]. Additionally a complicated multi-stage (six or more steps) synthesis is required to produce the bicyclic malonamides [71].

Another cyclic malonamide, i.e. the monocyclic 1,4-*bis*(cyclohexylmethyl)-1,4-diazepane-5,7-dione, have been studied only in the extraction reactions of U(VI) [47].



The effects of the substituents  $R_1$ ,  $R_2$ ,  $R_3$  (and  $R_4$ ) on extraction properties of malonamides can be thus divided in three groups [45, 57]:

1. The basicity of malonamides;
2. The geometry of malonamides and extracted complexes (e.g. the steric hindrance and the conformation effects);
3. The lipophilicity of malonamides and extracted complexes.

The substituents control both coordination of malonamides with metal ions (through basicity and geometry) and distribution of metal species between aqueous and organic phases (through lipophilicity).

#### 4.2.2 Coordination of malonamides with lanthanide(III) ions

The structure and composition of the nitrato complexes of trivalent lanthanides with malonamides have been the subject of a large number of investigations both in solid state [26, 58, 67, 68] and in solutions [67, 72-75].

##### A. Stoichiometry of nitrato complexes of trivalent lanthanides with malonamides

Usually the stoichiometry of complexes extracted into organic solutions is investigated by the slope analysis [7, 45]. By using this method the following lanthanide(III)-malonamide molar ratios in the extracted species were obtained: 1:2 [55, 56, 76-78], 1:3 [55, 61, 64, 77-80] and 1:4 [56, 78]. The results of the slope analysis greatly depend on experimental conditions, and often the slopes have non-integer values [45].

The alternative method for determination of stoichiometry of extracted species is the organic phase saturation by extraction [7]. The lanthanum(III)-malonamide ratio in the extracted complexes, measured by this method, was found to be 1:1.65 [45]. It was suggested that mixed complexes with the 1:1 and 1:2 ratios coexist in organic phase [45].

Vicentini *et al.* obtained the solid-state compounds of *N,N,N',N'*-tetramethylmalonamide (TMMA) with lanthanide(III) nitrates, which had the general formula  $[\text{Ln}(\text{NO}_3)_3(\text{TMMA})_2]$  [81, 82].

According to single-crystal X-ray diffraction data in all reported nitrato complexes of lanthanides(III) with malonamides the metal ion is coordinated with two molecules of malonamides [25, 26, 58, 66-68] except for three crystal structures, in which only one malonamide molecule is bonded to each lanthanide(III) ion and a saturation of the lanthanide(III) coordination spheres is accomplished by 1 – 3 water molecules [58, 83].

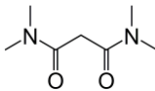
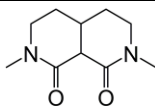
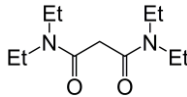
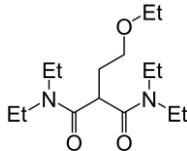
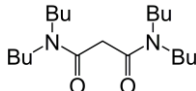
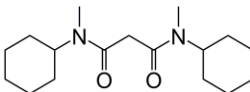
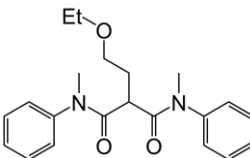
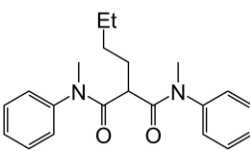
##### B. Coordination geometry of nitrato complexes of trivalent lanthanides with malonamides

There are 23 crystal structures of nitrato complexes of trivalent lanthanides (La, Pr, Nd, Eu, Gd, Yb) with malonamides in the Cambridge structural database (CSD, 2018) [25-27, 58, 66-68, 83-85]. In all these structures malonamides are bidentate ligands. Nitrates are bidentate and inner-sphere coordinate in all the structures except for  $[\text{Yb}(\text{NO}_3)_2(\text{NO}_3)(\text{TEMA})_2]$  with one monodentate nitrate [67], and  $[\text{Yb}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{Br-TEMA})(\text{NO}_3)]$  with one outer-sphere coordinate nitrate [83], where TEMA and Br-TEMA are *N,N,N',N'*-tetraethylmalonamide and 2-bromo-*N,N,N',N'*-tetraethylmalonamide, respectively.

In all three structures, containing ytterbium(III), the metal ion is nine-coordinate [58, 67, 83]. Lanthanides(III) are ten-coordinate in the rest twenty structures. Nineteen of these have one composition  $[\text{Ln}(\text{NO}_3)_3(\text{malonamide})_2]$  and the 1:2 lanthanide(III)-malonamide molar ratio, accordingly.

Regardless of a malonamide structure (Table 2) the average metal-carbonyl oxygen bond distances in the  $[\text{Ln}(\text{NO}_3)_3(\text{malonamide})_2]$  complexes with ten-coordinate lanthanides(III) are practically indistinguishable for the same metal.

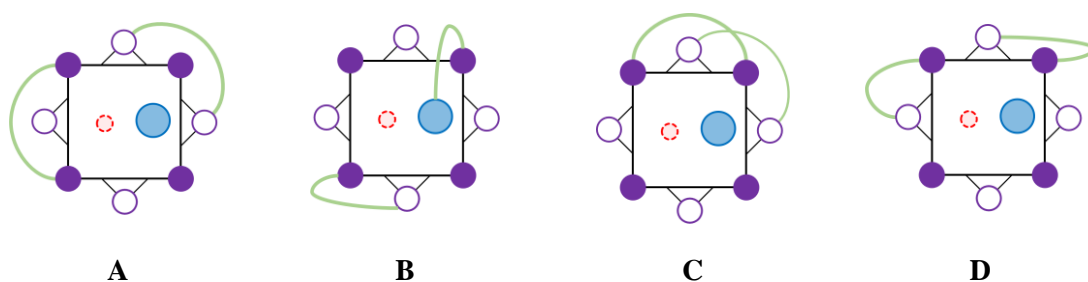
**Table 2** – The isomeric coordination polyhedra of lanthanides in bicapped square antiprism geometry (A, B, C or D from Fig. 7) identified for 18 crystal structures  $[\text{Ln}(\text{NO}_3)_3(\text{malonamide})_2]$  reported in the Cambridge structural database (CSD, 2018).

Malonamide		Isomeric type of coordination polyhedron of lanthanide(III)				
Abbreviation	Molecular structure	La	Pr	Nd	Eu	Gd
TMMA		<b>B</b> [25]	-	<b>B</b> [25]	<b>B</b> [25]	<b>D</b> [25]
DMBMA		<b>A</b> [25]	-	<b>D</b> [25]	<b>D</b> [25]	<b>C</b> [25]
TEMA		<b>A, A</b> [26, 68]	-	<b>A</b> [67]	-	-
TEEEMA		<b>D</b> [84]	-	-	-	-
TBMA		<b>A</b> [27]	<b>A</b> [85]	-	-	-
DMDCHMA		-	-	<b>A</b> [58]	-	-
DMDPEEMA		-	<b>D</b> [66]	<b>D</b> [66]	-	-
DMDPBMA		-	-	<b>D</b> [66]	-	-

Thus the lanthanum(III)-O(malonamide) average bond distances equal (in Å units): 2.502(4), 2.50(2) – 2.53(5), 2.48(2), 2.52(2) and 2.499(7) in the crystal structures with *N,N,N',N'*-tetramethylmalonamide (TMMA) [25], *N,N,N',N'*-tetraethylmalonamide (TEMA) [26, 68], *N,N,N',N'*-tetrabutylmalonamide (TBMA) [27], 2-(2-ethoxyethyl)-*N,N,N',N'*-tetraethylmalonamide (TEEEMA) [84] and 2,7-dimethylhexahydro-2,7-naphthyridine-1,8(2H,5H)-dione (DMBMA) [25]. Consequently it is unclear

from such XRD data if a molecular structure of malonamides (i.e. substituents  $R_1$ ,  $R_2$  and  $R_3$ ) affects their coordination with lanthanides(III).

The Cambridge structural database (CSD, 2018) was used for analyzing the stereochemistry of metal coordination in the polyhedra of eighteen crystal structures  $[Ln(NO_3)_3(malonamide)_2]$  with ten-coordinate lanthanides(III) (one structure [68] is unavailable in the CSD). All lanthanide(III) coordination polyhedra in these structures can be described as bicapped square antiprisms though some polyhedra are distorted. It was discovered that malonamides in the analyzed structures are arranged along various edges of bicapped square antiprisms in one of four distinct ways depicted schematically in Fig. 7. In other words four isomers of the lanthanide(III) coordination polyhedra were found in the crystal structures.



**Figure 7** – The schematic cap view of the isomeric coordination polyhedra of lanthanides in bicapped square antiprism geometry, observed in the  $[Ln(NO_3)_3(malonamide)_2]$  crystal structures. Dashed red and filled blue circles are the caps. A malonamide is shown as a green arch. Coordination of nitrates is omitted.

The isomers are listed in Table 2 for each structure. As one can see from Table 2 there are 7, 3, 1 and 7 crystal structures with the A, B, C and D isomeric coordination polyhedra of lanthanides, respectively. The type B isomers were observed only in the structures with TMMA. All four structures with  $R_3$ -substituents (excluding the complexes with DMBMA ligand) have the D isomers of the lanthanide coordination polyhedra. All six structure with  $R_3 = H$  have the A isomers, except for the complexes with TMMA (Table 2).

It is important to notice that the coordination polyhedra of lanthanides in the structures with one malonamide ligand can change along the lanthanide series, which may be used for an explanation of the lanthanide patterns (i.e. the dependencies of distribution ratios of lanthanide on their atomic numbers) in the extraction reactions [48, 76, 77, 79, 86].

It was assumed that the average intramolecular O-O distance between carbonyl oxygen atoms of two malonamide molecules in the crystal structures can be used as a parameter for a comparison of the coordination polyhedra isomers (Table 3). An intramolecular malonamide O-O contact is the edge of the coordination polyhedron (i.e. a bicapped square antiprism) in the crystal structures (Fig. 7). This distance should be the shortest in a complex with the strongest lanthanide(III)-malonamide chelate, which follows from a consideration of the malonamide conformers (Fig. 5). From this point of view the data in Table 3 indicate that the strength of binding between a lanthanide(III) and malonamides in the isomeric coordination polyhedra decreases in the order:  $B > D > A$ . Coordination polyhedra of the lanthanide(III) complexes with the bicyclic malonamides may deviate from this trend due to a rigid molecular framework of these ligands.

**Table 3** – The intramolecular O-O distances between carbonyl oxygen atoms of malonamides averaged for the crystal structures  $[Ln(NO_3)_3(malonamide)_2]$  with the same isomer of the lanthanide(III) coordination polyhedra (A, B and D from Fig. 7).

Isomer of coordination polyhedron	Average intramolecular malonamide O-O distance in lanthanide(III) coordination polyhedra, Å				
	La	Pr	Nd	Eu	Gd
<b>C</b>	-	-	-	-	2.768
<b>B</b>	2.729	-	2.707	2.688	-
<b>D</b>	2.775	2.789	2.788	2.764	2.791
<b>A</b>	2.831	2.807	2.799	-	-

For instance in the lanthanum(III) complexes the La(III)-malonamide binding strength should decrease in the order: TMMA > TEEEMA > TEMA as suggest by the data from Table 3. Rao *et al.* showed that the formation constants of the Eu(III) perchlorate complexes with the malonamides (Tables 1 and 2) in acetonitrile decrease in the order: TMMA > MTHMA > THMA (the FT-IR determined  $\log K = 2.48$ , 1.97 and 1.75, respectively) [60], where MTHMA is *N,N,N',N'*-tetrahexyl-2-methylmalonamide and THMA is *N,N,N',N'*-tetrahexylmalonamide. These data support the hypothesis of the intramolecular O-O distance effect if one considers THMA and MTHMA as the respective analogues of TEMA and TEEEMA (Table 2). Both TEEEMA and MTHMA are the  $R_3$ -alkyl substituted malonamides, while TEMA and THMA have bulkier  $R_1$  and  $R_2$  substituent than TMMA.

Coordination geometry of nitrato complexes of trivalent lanthanides with malonamides was studied in solutions by X-ray absorption spectroscopy (EXAFS, XANES) [67, 72, 74, 87]. Den Auwer *et al.* studied coordination of Nd, Eu, Ho, Yb and Lu with TEMA in ethanol and mixed methanol – ethanol solutions [67]. It was concluded that Nd, Eu and Ho are ten-coordinate in the complexes and bonded to three bidentate nitrates and two bidentate malonamides. In the complexes of Yb and Lu with TEMA both metal ions are nine-coordinate and bonded with two bidentate malonamides, one monodentate and two bidentate nitrates [67]. Gannaz *et al.* studied coordination of Nd, Eu and Yb with DMDOHEMA in *n*-dodecane [87]. It was established that these metal ions are eight-coordinate in the complexes, which were assumed to be composed of two bidentate molecules of DMDOHEMA and either one bidentate and two monodentate nitrates or three monodentate nitrates and one water molecule [87]. Ellis *et al.* studied coordination of Nd, Eu, Tb and Yb with DMDOHEMA in *n*-heptane [72] and coordination of Ce(III) with DMDBDTMA in *n*-dodecane [74]. The coordination numbers of lanthanides(III) in the complexes with the malonamides were found to be either eight (Ce, Tb and Yb) or nine (Nd and Eu) [72, 74]. An interesting observation was made regarding the denticities of nitrates in these complexes. Nitrates were estimated to be essentially monodentate in those malonamide complexes with lanthanides(III), which were dissolved in the organic phases saturated with nitric acid. They were bidentate in the complexes if the accommodating organic phase has not been contacted with the acid [72, 74].

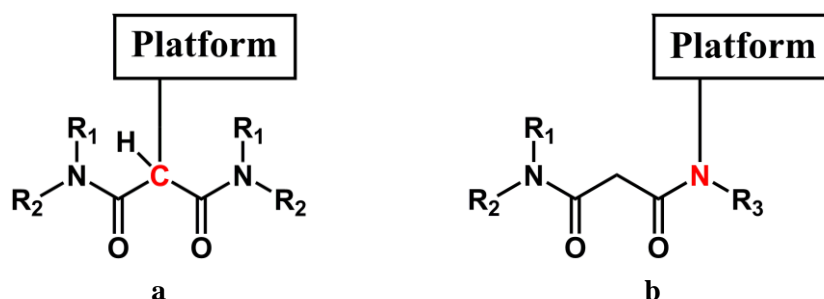
The theoretical aspects of coordination geometry of nitrato complexes of trivalent lanthanides with malonamides were studied by quantum mechanics calculations [88-90].

### 4.3 Ligands with multiple malonamide groups as extractants for lanthanides(III)

Commonly trivalent lanthanide ions have high coordination numbers (CN) both in solutions and in solid-state complexes ( $CN = 6 - 12$ ) [1, 91, 92]. For instance these numbers are eight and nine in the hydrated lanthanide(III) cations [92]. Therefore it has been argued by many researchers [11-17] that the polydentate solvent extraction ligands, often referred to as multicoordinate ligands [37], could extract lanthanides(III) with higher distribution ratios than low-dentate ligands due to the entropic effects [20]. The calixarenes are among the most known polydentate extraction ligands (e.g. [14]) engaged in trivalent actinide-lanthanide separation studies.

Polydentate extractants for lanthanides(III) can be prepared from water-soluble chelating polycarboxylic and aminopolycarboxylic acids, such as citric and nitrilotriacetic acids, by converting them into respective polyamides, which are insoluble or sparingly soluble in water [40, 93]. More often the polydentate extractants are assembled from two to four molecules of conventional solvent extraction ligands, such as diglycolamides [15], CMPO [94] *etc.*, chemically bonded by a linker called a platform [38] into one molecule. The number of ligating groups in the polydentate extractants usually matches the stoichiometric metal-ligand ratio in a complex of the metal with the corresponding conventional extractant.

Since the extracted complexes of conventional bidentate malonamides with trivalent lanthanides have the 1:2 or 1:3 metal-ligand ratios (e.g. [55, 56]), the polydentate extractants with two [11] and three [38, 39] malonamide functional groups (referred to as bis- and trismalonamides, respectively) were synthesized and investigated [11, 38, 39]. These ligands can be divided into the *C*- and *N*-alkylated polydentate malonamides according to the connection of malonamide ligating groups to a platform through either the bridging carbon atom or an amide nitrogen atom (Fig. 8), respectively, by the alkylation.

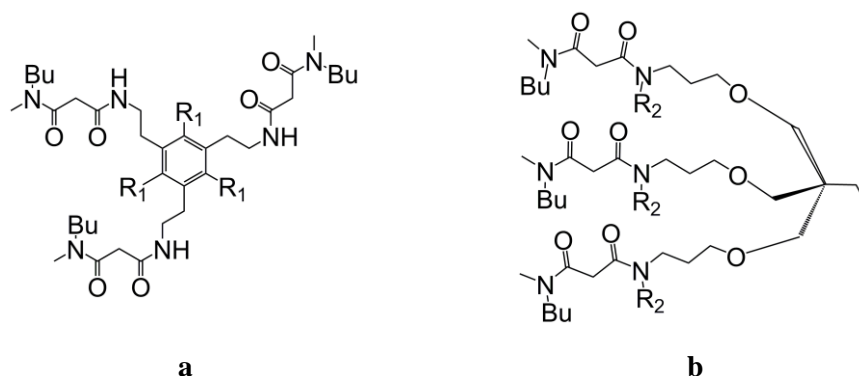


**Figure 8** – Two types of ligands with multiple malonamide ligating groups synthesized from bidentate malonamides by: **a** – *C*-alkylation; **b** – *N*-alkylation. A platform is a linker binding malonamide ligating groups into one molecule.

Both *C*- and *N*-alkylated bismalonamides were prepared [11], while only *N*-alkylated trismalonamides were reported [38, 39].

Janczewski *et al.* studied *N*-alkylated tripodal malonamide ligands (i.e. trismalonamides) with two types of a platform (Fig. 9) for solvent extraction of trivalent europium and americium [39]. The trismalonamides with platforms of type **a** (Fig. 9) have secondary and tertiary amides groups with di- and trialkylsubstituted nitrogen atoms, respectively. The distribution ratios of Am(III) and Eu(III) in the reactions with these trismalonamides were low and similar to those in the reactions with conventional malonamides [39]. The amide groups in the trismalonamides with platforms of type **b** (Fig. 9) are either tertiary or mixed (i.e. secondary and tertiary). The *N*-alkylation of secondary amide groups in these

trismalonamides with  $R_2$  substituents ( $R_2 = n\text{-C}_4\text{H}_9$ ,  $\text{C}_8\text{H}_{17}$  or  $\text{CH}(\text{C}_2\text{H}_5)_2$ ) had a negative effect on the extraction of trivalent f-block metals [39].



**Figure 9** – Molecular structures of the *N*-alkylated trismalonamides [39].  $R_1 = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ;  $R_2 = \text{H}$ ,  $n\text{-C}_4\text{H}_9$ ,  $\text{C}_8\text{H}_{17}$ ,  $\text{CH}(\text{C}_2\text{H}_5)_2$ .

Dam *et al.* studied the effects of a platform structure of *N*-alkylated trismalonamides (Table 4) on a trivalent actinide-lanthanide partitioning by extraction [38].

**Table 4** – Distribution ratios of  $\text{Eu(III)}$  in the reactions with the *N*-alkylated trismalonamides. The aqueous phase:  $10^{-3} \text{ M HNO}_3$ . Diluent of the organic phases: nitrobenzene. Data from Dam *et al.* [38].

Ligand number	Molecular structure of ligand	Ligand concentration, M	$D_{\text{Eu(III)}}$
I		0.01	0.34
II			0.69
III			2.12
IV		0.10	3.68
$\text{R} = \text{---} \text{CH}_2 \text{---} \text{C}(\text{O}) \text{---} \text{CH}_2 \text{---} \text{N}(\text{Bu})$			

The obtained data indicated that distribution ratios of Eu(III) depend on a platform structure of the trismalonamides (Table 4) [38].

Murillo *et al.* synthesized the series of the C- and N-alkylated bismalonamides (Tables 5 and 6) to investigate the effects of the alkylation type and a platform structure of these ligands on extraction of Am(III) and Eu(III) [11].

**Table 5** – The N-alkylated bismalonamides synthesized by Murillo *et al.* for solvent extraction of Am(III) and Eu(III) [11].

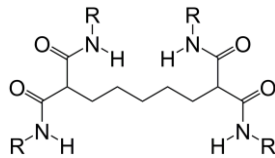
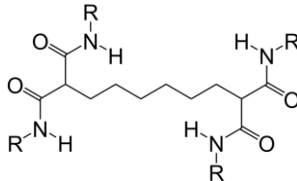
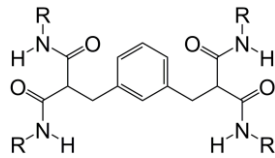
Platform	Ligand number	Molecular structure of ligand
phenylene	V	
	VI	
	VII	
xylylene	VIII	
	IX	

The distribution ratios of trivalent f-block metals in the reactions with some bismalonamides (e.g. ligand VIII, Table 5) in the chlorinated diluents (i.e. dichloromethane and 1,1,2,2-tetrachloroethane) were higher than in the reactions with DMDOHEMA. These better bismalonamides have a xylylene platform and were synthesized by N-alkylation of the malonamide ligating groups [11].

The bismalonamides, synthesized by Murillo *et al.* [11], contain either secondary amide groups (compounds V, X – XII, Tables 5 and 6) or both bridging secondary and terminal tertiary amide groups (compounds VI – IX, Table 5). Murillo *et al.* argues that secondary amides, in contrast to tertiary ones, do not induce adverse steric hindrance effects upon complexation with trivalent f-block metals [11]. However secondary amides have a disadvantage of being much less soluble in organic diluents than the respective tertiary amides. Thus, out of the twenty eight synthesized bismalonamides only three were

soluble in 1-octanol, and only one of those three was soluble in a 1:1 (by volume) mixture of 1-octanol and TPH (tetrapropylene hydrogenated) [11].

**Table 6** – The *C*-alkylated bismalonamides synthesized by Murillo *et al.* for solvent extraction of Am(III) and Eu(III) [11].

Platform	Ligand number	Molecular structure of ligand
pentylene	X	
hexylene	XI	
xylylene	XII	

The *C*-alkylation method of synthesis of ligands with multiple malonamide groups requires less expensive precursors than the *N*-alkylation one, which makes it more attractive for potential application in industry. The *C*-alkylated bismalonamides with tertiary amide groups have been synthesized for the first time in this dissertation work.



## 5. Experimental

### 5.1 Reagents and materials

All reagents for syntheses, solvent extraction and other experiments were purchased from Sigma-Aldrich, unless otherwise specified, and were at least 97 % pure with the exception of phthaloyl chloride, which was 90 % pure. All reagents were used as supplied.

The aliphatic kerosene Solvent 70, which contains hydrocarbons ( $C_{11} - C_{14}$ ), *n*-alkanes, isoalkanes, cyclics, and < 2 % aromatics, was purchased from Statoil Lubricants (Sweden).

The aromatic kerosene Solvesso 150 ND ( $C_{10}$ , aromatics, < 1 % naphthalene) was purchased from IsoChem AB (Sweden).

The solution of  $^{152}\text{Eu}$  in nitric acid ( $\text{pH} = 1$ ) was obtained from the existing stocks at Chalmers University of Technology (Gothenburg, Sweden).

The solutions of non-radioactive lanthanides(III) in nitric acid were prepared from the respective hydrated lanthanide(III) nitrates (Aldrich, 99.9 % trace metals basis), unless otherwise specified.

The stock solutions of lanthanide(III) perchlorates were obtained by dissolution of the respective lanthanide(III) oxides (Aldrich, 99.9 % trace metals basis) in perchloric acid (Aldrich, 70 %  $\text{HClO}_4$ , 99.999 % trace metals basis), followed by filtration of the solutions (25 mm syringe filter, w/0.45  $\mu\text{m}$  polypropylene membrane, VWR) and adjustment of acidities to  $\text{pH} = 1$ .

The volumetric solution of perchloric acid (1 M  $\text{HClO}_4$ , Fluka) and sodium perchlorate monohydrate (Aldrich, 99.99 % trace metals basis) were used to prepare the aqueous phases for solvent extraction experiments in perchlorate media.

The concentrated nitric acid (65 %, Suprapur<sup>®</sup>, Merck KGaA) was used for preparation of all aqueous phases for solvent extraction experiments in nitrate media and the matrices for ICP-MS analysis. Analytical standard solutions for ICP-MS analysis were purchased either from Ultra Scientific or LGC. The analytical standard solutions of lanthanides(III) and yttrium(III) were used for preparation of the aqueous phases for solvent extraction of the lanthanide series (excluding Pm).

The 0.01 M NaOH concentrate for 1 L standard solution was supplied by Fluka.

Deionized MilliQ water (Millipore, > 18.1  $\text{M}\Omega\cdot\text{cm}$  at 25 °C) was used for preparation of all aqueous solutions.

Liquid scintillation cocktail (Emulsifier-Safe<sup>™</sup> a high flash-point economy LSC-cocktail) and the glass tubes for liquid scintillation counting were supplied by Perkin-Elmer.

The nitric acid solution, containing dissolved irradiated nuclear fuel, was prepared as described previously [95]: the irradiated  $\text{UO}_2$  fuel (42  $\text{MW}\cdot\text{d}\cdot\text{kg}^{-1}$  U) from the rod No. 418-A6 of the boiling water reactor (BWR) Oskarshamn 1 (Sweden) was cut into 4.8 mm thick segments. Then a small piece of the  $\text{UO}_2$  pellet was dissolved in nitric acid (65 %, Suprapur<sup>®</sup>, Merck KGaA) by Dr. Stefan Allard at Chalmers University of Technology in 2014. The total U(VI) concentration in this stock was ( $1.52 \pm 0.03$ ) g/L according to the ICP-MS analysis.

Thin layer chromatography plates (TLC silica gel 60 F<sub>254</sub> plate) and high-purity silica gel (Grade 9385, particle size 40 - 63  $\mu\text{m}$ ) for flash chromatography were purchased from Merck KGaA.

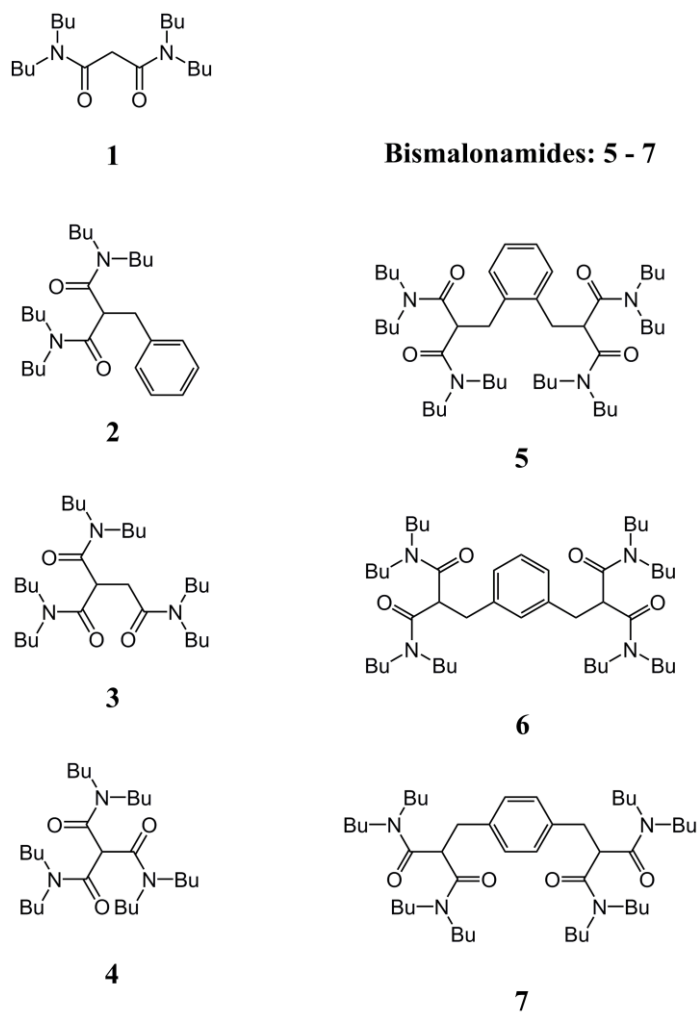
The scavenger resin *tris*(2-aminoethyl)amine (polymer bound, 200 – 400 mesh) was purchased from Aldrich.

All nuclear magnetic resonance (NMR) experiments were performed using 5 mm NMR tubes (Wilmad).

## 5.2 Syntheses

The ligands for the solvent extraction and single-crystal growth experiments as well as the precursors were synthesized. All synthesized compounds are denoted by numbers in the text for convenience. The purity of all synthesized compounds was at least (98 – 99) % (unless specified otherwise) and was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, CNH elemental microanalysis and in some cases by ESI-MS.

Molecular structures of the synthesized ligands used in the solvent extraction experiments are presented in Fig. 10.



**Figure 10** – Molecular structures of the synthesized ligands for solvent extraction. Bu stands for *n*-butyl ( $n\text{-C}_4\text{H}_9$ ).

### *Synthesis of N,N,N',N'-tetrabutylmalonamide (1)*

The diamide **1** was synthesized using a modification of the literature procedure [58]. Diethyl malonate (232 g, 1.45 mol) was mixed with *N,N*-dibutylamine (384 g, 2.97 mol). The mixture was heated to 160 °C and refluxed for 24 h. The extent of the reaction was monitored by thin layer chromatography (the mobile phase – 20 % v/v ethyl acetate in petroleum ether with b.p. 60 – 80 °C). The product was isolated by vacuum distillation as a pale yellow oil (351 g, 74 %; b.p. 156 °C at 1 mbar).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 (d,  $J = 2$  Hz, 2H), 3.28 (m, 8H), 1.50 (m, 8H), 1.28 (m, 8H), 0.89 (m, 12H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.70, 48.17, 45.76, 40.72, 31.04, 29.66, 20.17, 20.04, 13.83, 13.79 ppm. Anal. calcd. for  $\text{C}_{19}\text{H}_{38}\text{N}_2\text{O}_2$ : C, 69.89; H, 11.73; N, 8.58 %. Found: C, 69.38; H, 11.80; N, 8.54 %. IR ( $\text{cm}^{-1}$ ):

2959(vs), 2934(vs), 2873(s), 2733(w), 1743(w), 1637(vs), 1458(s), 1426(s), 1374(m), 1319(w), 1297(w), 1254(w), 1216(w), 1199(w), 1138(w), 1113(w), 1058(w), 1032(w), 942(m), 904(w), 881(w), 855(w), 783(w), 734(m), 649(w), 612(br. w), 522(br. w). The diamide **1** was used for syntheses of **2**, **3**, **5** - **7**.

#### *Synthesis of 2-benzyl-N,N,N',N'-tetrabutylmalonamide (2)*

Ligand **2** was synthesized from *N,N,N',N'*-tetrabutylmalonamide (**1**) and benzyl chloride in toluene by the reported method for synthesis of pentaalkylmalonamides [58]. The crude product was purified by flash chromatography with the cyclohexane – ethyl acetate (4:1) eluent [96]. The pure ligand **2** was obtained as a pale yellow oil (80 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (m, 12H), 1.25 (m, 8H), 1.44 (m, 8H), 3.24 (m, 10H), 3.85 (t, J = 6.8 Hz, 1H), 7.22 (m, 5H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 168.45, 139.79, 128.97, 128.36, 126.34, 109.99, 51.19, 47.32, 45.89, 35.82, 30.93, 29.42, 26.89, 20.23, 20.16, 13.89, 13.80 ppm. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.33 (dd, J = 8, 1.8 Hz, 2H), 7.07 (s, 2H), 6.98 (m, 1H), 3.99 (m, 1H), 3.45 (m, 2H), 3.15 (m, 8H), 1.45 (m, 4H), 1.13 (m, 12H), 0.78 (m, 12H) ppm. <sup>13</sup>C NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 168.07, 140.46, 129.18, 128.22, 126.21, 53.35, 46.92, 45.58, 35.80, 30.91, 29.56, 20.16, 19.99, 13.73, 13.62 ppm. Anal. calcd. for C<sub>26</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>: C, 74.95; H, 10.64; N, 6.72 %. Found: C, 74.53; H, 10.73; N, 6.62 %.

#### *Synthesis of N,N,N',N',N'',N''-hexabutylethane-1,1,2-tricarboxamide (3)*

Sodium hydride (1.27 g of a 60 % dispersion in mineral oil, 30.6 mmol) was washed with petroleum ether and suspended in toluene (100 cm<sup>3</sup>) under a nitrogen atmosphere. The diamide **1** (10.04 g, 30.6 mmol) was added and the mixture was stirred at 100 °C until hydrogen evolution had ceased (*ca.* 1 h). *N,N*-dibutyl-2-chloroacetamide (**12**) (6.31 g, 30.6 mmol) was then added dropwise and the mixture was refluxed for 24 h. After cooling, water (50 cm<sup>3</sup>) was added with care to the reaction mixture. After drying over sodium sulfate and removal of solvent the crude product was purified using flash chromatography with petroleum ether – ethyl acetate (4:1) as eluent [96]. The pure triamide **3** was obtained as a pale yellow oil (3.12 g, 20 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.36 (m, 1H), 3.22 (m, 12H), 2.81 (d, J = 5.5 Hz, 2H), 1.52 (m, 12H), 1.26 (m, 12H), 0.88 (m, 18H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 169.88, 169.07, 47.85, 47.54, 46.23, 45.69, 44.36, 32.96, 31.16, 30.96, 29.85, 29.44, 20.22, 20.18, 20.14, 20.11, 13.85, 13.78 ppm. Anal. calcd. for C<sub>29</sub>H<sub>57</sub>N<sub>3</sub>O<sub>3</sub>: C, 70.26; H, 11.59; N, 8.47 %. Found: C, 70.43; H, 11.72; N, 8.30 %. IR (cm<sup>-1</sup>): 2959(vs), 2933(s), 2873(vs), 1652(vs), 1456(s), 1426(s), 1378(m), 1294(w), 1255(w), 1200(w), 1137(m), 1114(w), 980(w), 957(w), 933(w), 904(vw), 784(br. w), 734(m), 603(br. w), 566(br. w), 527(br. w).

#### *Synthesis of N,N,N',N',N'',N''-hexabutylmethanetricarboxamide (4)*

The triamide **4** was prepared using the reported method for synthesis of the homologous triamides [97]. The product was obtained as a white solid and was purified by recrystallization from petroleum ether (b.p. 60 – 80 °C) (21.62 g, 69 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.60 (s, 1H), 3.29 (br. s, 6H), 3.09 (m, 6H), 1.54 (m, 12H), 1.29 (m, 12H), 0.91 (m, 18H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 164.93, 47.94, 46.19, 31.05, 29.19, 20.27, 20.22, 13.88, 13.83 ppm. Anal. calcd. for C<sub>28</sub>H<sub>55</sub>N<sub>3</sub>O<sub>3</sub>: C, 69.81; H, 11.51; N, 8.72 %. Found: C, 69.80; H, 11.77; N, 8.80 %. IR (cm<sup>-1</sup>): 2959(vs), 2929(vs), 2872(vs), 1637(vs), 1472(vs), 1440(vs), 1376(m), 1307(m), 1294(m), 1221(w), 1209(s), 1139(s), 1118(m), 1054(w), 1007(w), 909(m), 907(m), 867(w), 795(w), 735(s), 709(m), 633(s), 606(m), 521(s).

#### *Synthesis of 2,2'-(1,2-phenylenebis(methylene))bis(N,N,N',N'-tetrabutylmalonamide) (5)*

The tetraamide **5** was prepared from *N,N,N',N'*-tetrabutylmalonamide (**1**) and 1,2-bis(bromomethyl)benzene as the alkylating reagent in tetrahydrofuran (THF) by the method used for synthesis of the triamide **3** omitting the stage of the product purification by flash chromatography. The

product was obtained as an orange oil (27.88 g, 94 %), which slowly solidified (m.p. 51 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.04 (m, 4H), 4.02 (t, J = 7.2 Hz, 2H), 3.24 (m, 12H), 2.96 (m, 8H), 1.34 (m, 32H), 0.88 (m, 24H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 168.63, 137.45, 129.53, 126.65, 47.67, 47.31, 45.81, 32.94, 30.61, 29.35, 20.30, 20.20, 13.83, 13.76 ppm. Anal. calcd. for C<sub>46</sub>H<sub>82</sub>N<sub>4</sub>O<sub>4</sub> (M<sub>r</sub> = 754.63): C, 73.16; H, 10.94; N, 7.42 %. Found: C, 72.69; H, 10.96; N, 7.24 %. ESI-MS (CH<sub>3</sub>CN): *m/z* = 755.61 [L + H]<sup>+</sup>, 777.59 [L + Na]<sup>+</sup>. IR (cm<sup>-1</sup>): 2955(br. vs), 2862 (br. vs), 2735(w), 1944(vw), 1635(br. vs), 1456(br. vs), 1421(br. vs), 1374(br. vs), 1289(br. vs), 1255(br. vs), 1200(br. vs), 1133(br. s), 1069(m), 1044(w), 955(s), 933(s), 903(m), 840(w), 751(vs), 658(s), 604(w), 570(m), 560(m), 509(br. m).

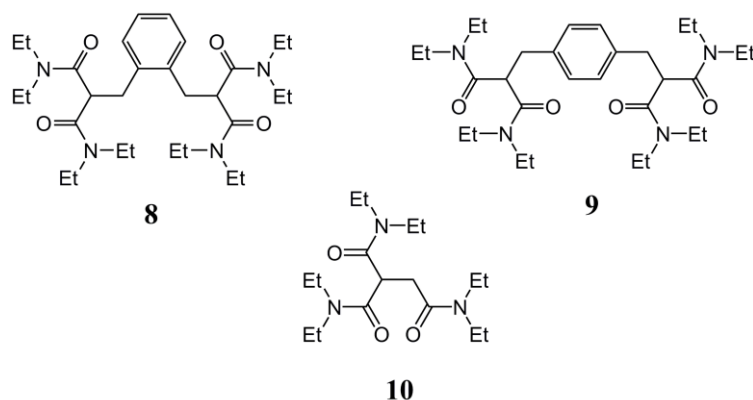
*Synthesis of 2,2'-(1,3-phenylenebis(methylene))bis(N,N,N',N'-tetrabutylmalonamide) (6)*

Bismalonamide **6** was prepared from *N,N,N',N'*-tetrabutylmalonamide (**1**) and 1,3-*bis*(bromomethyl)benzene as the alkylating reagent by the method used for synthesis of bismalonamide **5**. Residual 1,3-*bis*(bromomethyl)benzene and traces of 2-(3-(bromomethyl)benzyl)-*N,N,N',N'*-tetrabutylmalonamide were removed from the crude product by the contact with the scavenger resin *tris*(2-aminoethyl)amine in tetrahydrofuran (THF) (1 g resin per 1 g crude product in 25 mL THF, room temperature, stirring for 24 h) [98]. Ligand **6** was isolated as a brown oil (86 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (m, 4H), 3.69 (m, 2H), 3.16 (m, 20H), 1.31 (m, 32H), 0.82 (m, 24H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 168.46 139.80, 129.72, 128.48, 126.98, 50.58, 47.31, 45.81, 35.84, 30.83, 29.39, 20.20, 20.13, 13.85, 13.76 ppm. Anal. calcd. for C<sub>46</sub>H<sub>82</sub>N<sub>4</sub>O<sub>4</sub> (M<sub>r</sub> = 754.63): C, 73.16; H, 10.94; N, 7.42 %. Found: C, 71.15; H, 10.59; N, 7.05 %. ESI-MS (CH<sub>3</sub>CN): *m/z* = 755.61 [L + H]<sup>+</sup>, 777.60 [L + Na]<sup>+</sup>. ATR-FTIR (wavenumber, cm<sup>-1</sup>): 2960 (s), 2930 (s), 2870 (m), 1630 (vs), 1440 (s), 1420 (vs), 1380 (m), 1290 (w), 1260 (w), 1220 (m), 1200 (m), 1130 (m), 1110 (w), 933 (w), 901 (vw), 789 (w), 735 (m), 704 (m), 658 (w). Bismalonamide **6** contains 4.5 % (mas.) THF (the solvent): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.78, 1.80 ppm; <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 67.89, 25.55 ppm [99].

*Synthesis of 2,2'-(1,4-phenylenebis(methylene))bis(N,N,N',N'-tetrabutylmalonamide) (7)*

Bismalonamide **7** was prepared from *N,N,N',N'*-tetrabutylmalonamide (**1**) and 1,4-*bis*(bromomethyl)benzene as the alkylating reagent by the method used for synthesis of bismalonamide **6**. Ligand **7** was isolated as a pale yellow waxy solid (71 % yield); m.p. (52-55) °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86 (m, 24H), 1.21 (m, 16H), 1.39 (m, 16H), 3.20 (m, 20H), 3.77 (m, 2H), 7.08 (m, 4H) ppm. <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>) δ 13.78, 13.85, 20.14, 20.19, 29.37, 30.91, 35.29, 45.85, 47.33, 50.81, 128.90, 137.79, 168.47 ppm. Anal. calcd. for C<sub>46</sub>H<sub>82</sub>N<sub>4</sub>O<sub>4</sub> (M<sub>r</sub> = 754.63): C, 73.16; H, 10.94; N, 7.42 %. Found: C, 72.58; H, 10.67; N, 7.36 %. ESI-MS (CH<sub>3</sub>CN): *m/z* = 755.62 [L + H]<sup>+</sup>, 777.60 [L + Na]<sup>+</sup>. ATR-FTIR (wavenumber, cm<sup>-1</sup>): 2960 (s), 2930 (s), 2870 (m), 1650 (vs), 1630 (vs), 1510 (vw), 1460 (br. s), 1420 (vs), 1370 (m), 1300 (w), 1270 (w), 1260 (w), 1220 (m), 1200 (m), 1190 (m), 1130 (m), 1110 (m), 1050 (vw), 1020 (vw), 945 (m), 901 (vw), 852 (vw), 827 (m), 731 (m), 706 (vw), 652 (w), 613 (m), 571 (m). Bismalonamide **7** contains traces of the THF solvent < 2 % (mas.) [99].

Molecular structures of the synthesized ligands used in the single-crystal growth experiments are presented in Fig. 11.



**Figure 11** – Molecular structures of the synthesized ligands for single-crystal growth. Et stands for ethyl ( $C_2H_5$ ).

*Synthesis of 2,2'-(1,2-phenylenebis(methylene))bis(N,N,N',N'-tetraethylmalonamide) (8)*

Tetraamide **8** was synthesized from *N,N,N',N'*-tetraethylmalonamide (**13**) and 1,2-*bis*-(bromomethyl)benzene in tetrahydrofuran as previously described for **5**. Ligand **8** was isolated as a pale brown solid (64 % yield); m.p. (78-79) °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.99 (t,  $J$  = 7 Hz, 12H), 1.06 (t,  $J$  = 7.2 Hz, 12H), 3.00 (m, 4H), 3.14 (m, 4H), 3.25 (m, 8H), 3.37 (m, 4H), 4.09 (t,  $J$  = 7.2 Hz, 2H), 7.06 (m, 4H) ppm.  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  168.5, 137.3, 129.6, 126.6, 47.4, 41.3, 40.1, 33.0, 13.6, 12.6 ppm. ATR-FTIR (wavenumber,  $cm^{-1}$ ): 2970(br. w), 2933(br. w), 2873(vw), 1639(s), 1620(br. vs), 1496(w), 1468(m), 1442(s), 1427(br. s), 1377(m), 1361(m), 1327(w), 1323(vw), 1309(w), 1281(m), 1263(m), 1244(vw), 1215(m), 1171(vw), 1146(w), 1126(m), 1090(br. m), 1041(vw), 1011(br. vw), 972(w), 955(m), 916(vw), 879(w), 860(w), 833(w), 764(br. m), 758(s), 708(vw), 710(vw), 665(w), 627(vw), 611(m), 580(m). Anal. calcd. for  $C_{30}H_{50}N_4O_4$ : C, 67.89; H, 9.50; N, 10.56 %. Found: C, 67.29; H, 9.85; N, 10.35 %.

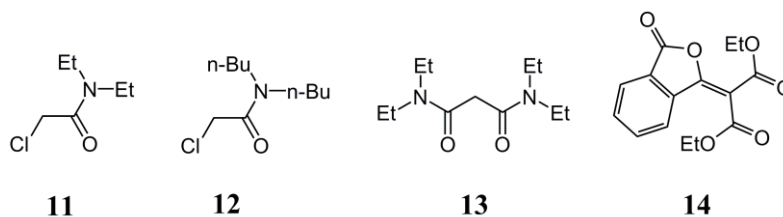
*Synthesis of 2,2'-(1,4-phenylenebis(methylene))bis(N,N,N',N'-tetraethylmalonamide) (9)*

Tetraamide **9** was synthesized from *N,N,N',N'*-tetraethylmalonamide (**13**) and 1,4-*bis*-(bromomethyl)benzene in tetrahydrofuran by the method used for synthesis of **8**. Compound **9** was isolated as a white solid (89 % yield); m.p. 138 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.1 (s, 4H), 3.78 (t,  $J$  = 6.8 Hz, 2H), 3.25 (m, 20H), 1.05 (m, 24H) ppm.  $^{13}C$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  168.23, 137.65, 129.06, 50.82, 41.38, 40.31, 35.43, 13.88, 12.61 ppm. Anal. calcd. for  $C_{30}H_{50}N_4O_4$ : C, 67.89; H, 9.50; N, 10.56 %. Found: C, 67.14; H, 9.60; N, 10.36 %.

*Synthesis of N,N,N',N',N'',N''-hexaethylethane-1,1,2-tricarboxamide (10)*

The triamide **10** was prepared from *N,N,N',N'*-tetraethylmalonamide (**13**) and 2-chloro-*N,N*-diethylacetamide (**11**) by the method used for synthesis of **3**. The product was obtained as a brown oil (96 % yield) without using flash chromatography for purification.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  4.37 (t,  $J$  = 6.3 Hz, 1H), 3.34 (m, 12H), 2.84 (d,  $J$  = 6.3 Hz, 2H), 1.15 (br. m, 18H) ppm.  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  169.67, 168.72, 44.15, 42.12, 41.76, 40.66, 40.34, 32.89, 14.31, 14.11, 13.05, 12.72 ppm.  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  169.29, 168.45, 44.66, 41.64, 41.29, 40.31, 39.94, 33.08, 13.92, 13.76, 12.93, 12.65 ppm. Anal. calcd. for  $C_{17}H_{33}N_3O_3$ : C, 62.35; H, 10.16; N, 12.83 %. Found: C, 61.55; H, 10.52; N, 12.79 %.

Molecular structures of the synthesized precursors and diethyl 2-(3-oxoiso-1,3-dihydrobenzofuran-1-ylidene)malonate are presented in Fig. 12.



**Figure 12** – Molecular structures of the synthesized precursors **11** – **13** and diethyl 2-(3-oxoisobenzofuran-1-ylidene)malonate (**14**).

#### *Synthesis of 2-chloro-N,N-diethylacetamide (**11**)*

The precursor **11** was prepared by reacting 2-chloroacetyl chloride with diethylamine as reported for synthesis of an amide from acid chlorides and amines [31]. The pure product was obtained as a pink oil (87 % yield) without vacuum distillation.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.01 (s, 2H), 3.32 (m, 4H), 1.18 (t,  $J$  = 7.2 Hz, 3H), 1.08 (t,  $J$  = 7 Hz, 3H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  165.61, 42.40, 41.26, 40.53, 14.33, 12.60 ppm.

#### *Synthesis of 2-chloro-N,N-dibutylacetamide (**12**)*

The precursor **12** was prepared by the method used for synthesis of **11**. The crude product was distilled in vacuum to yield a yellow oil (56 % yield; b.p. (122-128) °C at 5 mbar).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.98 (d,  $J$  = 1.6 Hz, 2H), 3.21 (m, 4H), 1.47 (m, 4H), 1.25 (m, 4H), 0.85 (m, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  165.90, 47.95, 45.87, 41.26, 31.11, 29.37, 20.02, 19.66, 13.74, 13.67 ppm.

#### *Synthesis of N,N,N',N'-tetraethylmalonamide (**13**)*

The precursor N,N,N',N'-tetraethylmalonamide was synthesized by reacting malonyl chloride with diethylamine [5] and purified by vacuum distillation (b.p. 116-118 °C at 1 mbar). The product was collected as a pale yellow oil (39 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.38 (m, 10H), 1.16 (t,  $J$  = 7.2 Hz, 6H), 1.10 (t,  $J$  = 7 Hz, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  166.33, 42.58, 40.65, 40.28, 14.13, 12.85 ppm. The NMR spectra of **13** obtained are in agreement with those reported in the literature [30].

#### *Synthesis of diethyl 2-(3-oxoisobenzofuran-1-ylidene)malonate (**14**)*

The compound  $\text{C}_{15}\text{H}_{14}\text{O}_6$  (**14**) was prepared by the reaction of diethyl malonate with phthaloyl chloride in acetonitrile in the presence of triethylamine and magnesium chloride [100]. The crude product was washed with petroleum ether on the paper filter and recrystallized from cyclohexane as colorless crystals (69 % yield); m.p. (72-73) °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.38 (m, 6H), 4.39 (m, 4H), 7.72 (t,  $J$  = 6.7 Hz, 1H), 7.80 (t,  $J$  = 7.4 Hz, 1H), 7.99 (d,  $J$  = 7.8 Hz, 1H), 8.65 (d,  $J$  = 8.2 Hz, 1H) ppm.  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  135.36; 132.93; 127.58; 126.11; 125.84; 62.18; 62.06; 14.04; 14.01 ppm. Anal. calcd. for  $\text{C}_{15}\text{H}_{14}\text{O}_6$ : C, 62.07; H, 4.86 %. Found: C, 62.08; H, 4.94 %. The crystalline product was found to be stable to air, water and brief exposure to 1 M hydrochloric acid.

Based on the search in the Reaxys® and SciFinder® databases, conducted in May 2018, it was concluded that the compounds **2** – **10** are novel and have not been reported previously.

### **5.3 Solvent extraction**

All solvent extraction experiments were conducted in 2 mL glass vials with polyethylene caps using an IKA VIBRAX VXR Basic® vibration stirrer (1500 rpm), equipped with thermostatic cells, for a phase contact.

Organic and aqueous phases were not pre-equilibrated in the spike extraction tests with  $^{152}\text{Eu}$ . In these tests equal volumes (300  $\mu\text{L}$ ) of two phases were contacted at  $(25.0 \pm 0.1)^\circ\text{C}$ . The radioactivity of  $^{152}\text{Eu}$  in aqueous phases varied from 0.6 kBq/mL ( $0.6 \cdot 10^{-9}$  M) to 3 kBq/mL ( $0.3 \cdot 10^{-8}$  M).

The  $\beta$  radioactivity of the 50  $\mu\text{L}$  aliquots from aqueous phases before and after extraction was measured in the liquid scintillation cocktail (5 mL) using the liquid scintillation counter (LSC).

The extraction of nitric acid was studied separately by contacting 300  $\mu\text{L}$  of an organic phase with 600  $\mu\text{L}$  of an aqueous phase. Concentrations of nitric acid in the aqueous phases before and after the acid extraction were determined by volumetric titration of the respective aliquots (300  $\mu\text{L}$ ).

In all experiments on solvent extraction of non-radioactive metals both aqueous and organic phases were pre-equilibrated, unless otherwise specified. The pre-equilibration was conducted at room temperature  $(22 \pm 1)^\circ\text{C}$  for 30 min. Aqueous phases were pre-equilibrated by contacting with a diluent of an organic phase alone. Equal volumes (400 – 600  $\mu\text{L}$ ) of the pre-equilibrated aqueous and organic phases were used for extraction.

The metal concentrations in aqueous phases varied from 0.4  $\mu\text{M}$  to 6 mM. The (50 – 150)  $\mu\text{L}$  aliquots of the aqueous phases before and after extraction of metals were dissolved in nitric acid with the dilution factors (1:10000) – (1:100), and the prepared samples were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS).

In all solvent extraction experiments a disengagement of two phases after the contact was facilitated by centrifugation (Heraeus Labofuge 200, 3000 – 5000 rpm, 3 – 5 min) with an exception of the experiments in which methyl isobutyl ketone (MIBK) was used as a diluent of an organic phase and a centrifugation was not required due to a rapid phase separation.

All solvent extraction experiments were performed in triplicate. The reported distribution ratios (D) are the mean of those calculated for three repeated experiments.

In the experiments on solvent extraction of radioactive  $^{152}\text{Eu}$  the radioactivity of the aqueous phases was used instead of concentrations to calculate the distribution ratios of europium(III).

#### 5.4 Preparation of single-crystal complexes of lanthanides with the synthesized ligands

Ligands **8** - **10** were used for growing single-crystal complexes with lanthanide(III) nitrates and perchlorates. The single-crystal structures, suitable for X-ray diffraction analysis, were obtained only with bismalonamide **8**, which is denoted as L further in the text for convenience. The crystal structures  $[\text{Nd}_2(\text{NO}_3)_6\text{L}_2] \cdot (\text{CH}_3\text{CN})_3$  (**15**),  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2] \cdot [\text{Nd}(\text{NO}_3)_5] \cdot (\text{CH}_3\text{CN})_{1.5}$  (**16**) and  $\text{Ce}(\text{NO}_3)_3\text{L}_2$  (**17**) were obtained by the following method. The trinitrate hydrated salt of a respective lanthanide and ligand **8** were dissolved in acetonitrile ( $\text{CH}_3\text{CN}$ ) separately to give 0.5 M and 1 M solutions of Ln(III) and the ligand, respectively. Equal volumes (1 mL) of the two solutions were combined in a 20 mL glass vial equipped with a screw cap. The mixture was left overnight in a closed vial. The vial, without a cap, was then placed in a 100 mL glass vessel filled with *ca.* 10 mL of diethyl ether. The vessel was sealed with a plastic lid and crystals were obtained by solvent vapor diffusion at room temperature  $(23 \pm 2)^\circ\text{C}$  over *ca.* 24 h. Crystals of **15** and **16** were harvested from the same vial. A similar method was used to prepare crystals of  $[\text{NdL}_2] \cdot (\text{ClO}_4)_3 \cdot \text{C}_2\text{H}_5\text{OH}$  (**18**). In this case the metal and the ligand concentrations were reduced to *ca.* 0.25 M and 0.5 M, respectively, and a 1:1 (v/v) mixture of acetonitrile and ethanol was used as a solvent. Neodymium(III) perchlorate was obtained by reacting  $\text{Nd}_2\text{O}_3$  (0.1269 g) with perchloric acid (0.4 mL, 70 %  $\text{HClO}_4$ ) followed by dissolution in the acetonitrile-ethanol solvent and filtration with a syringe filter (25 mm, w/0.45  $\mu\text{m}$  polypropylene membrane).

## 5.5 Stoichiometry of the bismalonamide complexes with lanthanides(III) in solutions

The stoichiometry of the bismalonamide **8** complexes with Nd(III) and Pr(III) nitrates was studied in acetonitrile solutions by electrospray ionization – mass spectrometry (ESI-MS). The samples with the 1:1 and 1:2 metal-to-ligand molar ratios were prepared by dissolution of the ligand **8** and the respective metal salt  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in acetonitrile ( $[\text{Ln(III)}] = 1 \text{ mg/mL}$ ). Acetic acid was added to the samples (0.1 % vol.) before the analysis. The ESI-MS spectrum of the ligand in acetonitrile ( $[\text{L}] = 2 \text{ mg/mL}$ ; 0.1 % vol.  $\text{CH}_3\text{COOH}$ ) was recorded separately. The samples, diluted with acetonitrile to 10  $\mu\text{g/mL}$  Ln(III), were used to record high-resolution mass spectra.

## 5.6 Analytical techniques

### A. Nuclear magnetic resonance spectroscopy (NMR)

All nuclear magnetic resonance experiments ( $^1\text{H}$  and  $^{13}\text{C}$ , 400 MHz) were performed using an Agilent400-VNMRS400 (400 MHz) spectrometer supplied by Agilent.

### B. Electrospray ionization – mass spectrometry (ESI-MS)

The electrospray ionization – mass spectrometry (ESI-MS) measurements were conducted on a unit mass LC-MS instrument (Agilent 1260 HPLC and 6120 single quadrupole) equipped with an electrospray interface operated in positive ionization mode. The samples were analyzed by flow injection ESI-MS using the sample solvent (i.e. acetonitrile) as the carrier (flow rate – 0.2 mL/min; injection volume – 1  $\mu\text{L}$ ). Spectra were acquired over a mass range of  $m/z = (300 - 2000)$ . High-resolution mass spectra were obtained by direct infusion of the sample into the positive ESI ion source of the mass spectrometer (Agilent 6520) using a syringe pump (flow rate – 300  $\mu\text{L/hour}$ ).

### C. Liquid scintillation counting (LSC)

All liquid scintillation counting measurements were performed in 7 mL glass tubes using a Wallac 1414 Guardian liquid scintillation counter (LSC) supplied by Perkin-Elmer. The counting time per tube was 30 minutes.

### D. Infra-red spectroscopy (IR)

The infra-red spectra of ligands **1**, **3** and **4** were collected using a Perkin-Elmer Spectrum Two FT-IR spectrometer. The resolution was set to  $2 \text{ cm}^{-1}$  and 16 scans of each sample were used to create the spectrum. Solid samples were ground with potassium bromide before being pressed into a disk. Liquid samples were studied in the form of thin films of the liquid between potassium bromide disks. The infra-red spectra of bismalonamide ligands **5** - **8** were collected using a Nicolet 6700 FT-IR spectrometer (Thermo Scientific), equipped with a diamond attenuated total reflectance (ATR) cell. The resolution was set to  $4 \text{ cm}^{-1}$  and 64 scans of a sample were made for the FTIR spectrum recorded. When reporting infrared spectrum the following abbreviations were used to indicate the intensity of the absorption peaks: v – very, br – broad, m – moderate, s – strong and w – weak.

### E. Single-crystal X-ray diffraction

All single-crystal X-ray diffraction measurements were made by Prof. Alexandra M.Z. Slawin and Dr. David B. Cordes at the University of St. Andrews (Great Britain) on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated  $\text{Mo-K}\alpha$  radiation (wavelength  $0.71075 \text{ \AA}$ ). The collected reflections were processed using *CrystalClear-SM Expert 2.1 b32* (Rigaku) for the structure **14** [101], *CrystalClear* (Rigaku) [102] for the structures **15**, **16**, **18**, and *CrysAlis PRO* 1.171.38.43i (Rigaku Oxford Diffraction) [103] for the structure **16**. Empirical absorption corrections were applied to the linear absorption coefficients  $\mu$  of the structures **14**, **15**, **17** and **18**, and the data were corrected



for Lorentz and polarization effects. The spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, were used for correction of  $\mu$  of the structure **16**. The structure  $C_{15}H_{14}O_6$  (**14**) was solved by direct methods [104] and expanded using Fourier techniques. Table A1 contains selected crystallographic data and refinement details for the crystal structure **14**. The structure **15** was solved by heavy-atom Patterson methods [105] and expanded using Fourier techniques. The structure **16** was solved by structure-invariant direct methods and expanded using Fourier techniques. The structures **17** and **18** were solved by direct methods [104] and [106], respectively, and expanded using Fourier techniques. Table A2 contains selected crystallographic data and refinement details for the crystal structures **15** - **18**. Neutral atom scattering factors were taken from International Tables for Crystallography [107]. Anomalous dispersion effects were included in  $F_{\text{calc}}$  [108]; the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley [109]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [110]. All calculations were performed using the CrystalStructure [111] crystallographic software package except for refinement, which was performed using SHELXL2013 [112] for the structure **15** and SHELXL Version 2014/7 [112] for the structures **16** - **18**. In the crystal structures **14** - **18** the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model.

#### *F. Inductively coupled plasma–mass spectrometry (ICP-MS)*

Concentrations of metal ions in aqueous solutions were measured by the external standard method [113] with an iCAP Q inductively coupled plasma–mass spectrometer (Thermo Scientific). The matrices for ICP-MS analyses contained 1 mol/L nitric acid and 1 ppb Rh or Ru as an internal standard.

The intensities of the isotope signals were used instead of their analytical concentrations for calculating the distribution ratios in the samples, containing dissolved spent nuclear fuel, since the external calibration method is not applicable for the analysis of most of the radioactive isotopes by ICP-MS. The intensities of the signals of the isotopes with the mass numbers 234 – 241, 243 and 244 were measured in the kinetic energy discrimination (KED) mode to eliminate possible interferences from the polyatomic species such as  $UH^+$ .

#### *G. Elemental analysis*

The CNH elemental analysis, i.e. the determination of the mass fractions of the C, N and H atoms in the samples of the synthesized reagents, was performed by Medac Ltd (Great Britain).

#### *H. Acid-base volumetric titration*

Concentrations of nitric acid in the aqueous phases before and after the acid extraction were determined by volumetric titration with 0.01 M NaOH standard solution using phenolphthalein as the indicator.

#### *I. Melting point measurements*

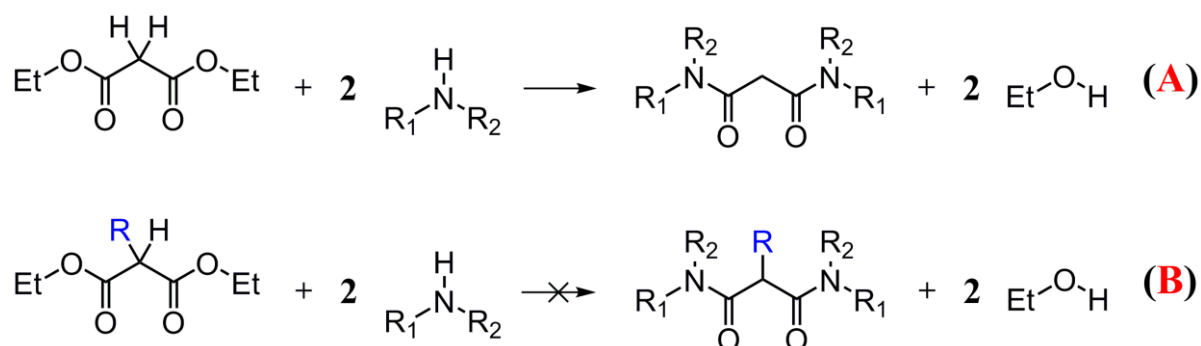
Melting points of the solid ligands were determined in glass capillaries using a Gallenkamp Melting Point Apparatus equipped with a liquid in glass thermometer.

## 6. Results and discussion

### 6.1 Syntheses of the amides

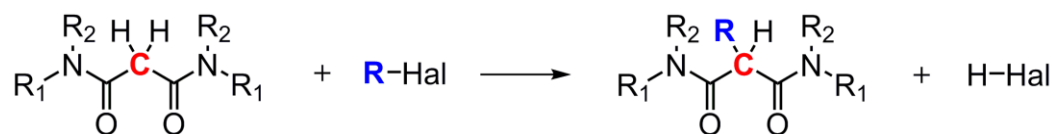
The amides **1** – **13** (Fig. 10 – 12) were synthesized in this work. The amides **11** – **13** (Fig. 12) were synthesized by the amidation of the amines with the respective acyl chlorides. The acid esters were used to prepare the amides **1** and **4** (Fig. 10). The synthesis of **4** required the presence of the catalyst 2-hydroxypyridine [97]. In the synthesis of *N,N,N',N'*-tetraethylmalonamide (**13**) malonyl chloride (the acyl chloride) was selected as the amidating reagent instead of diethyl malonate (the acid ester) due to low boiling point of diethylamine (b.p. 55° C), which does not allow to convert diethyl malonate (b.p. 199° C) into the amide **13** by heating it under reflux with diethylamine<sup>7</sup>.

Dul *et al.* demonstrated that, in contrast to *N,N,N',N'*-tetraalkylmalonamides, the malonamides with the alkyl-substituted carbon atom, bridging two carbonyl groups, cannot be synthesized by the reaction of the respective ester (i.e. diethyl 2-alkylmalonate) with amine (Fig. 13) [63].



**Figure 13** – The schemes of the reactions of a dialkylamine with diethyl malonate (A) and diethyl 2-alkylmalonate (B). R, R<sub>1</sub> and R<sub>2</sub> are alkyl substituents. Et stands for ethyl (C<sub>2</sub>H<sub>5</sub>).

For this reason the amides **2**, **3**, **5** – **10** (Fig. 10 and 11), the molecules of which contain the malonamide functional groups (either one or two) substituted at the bridging carbon atom, were synthesized by the C-alkylation of the corresponding *N,N,N',N'*-tetraalkylmalonamides (**1** or **13**) (Fig. 14).



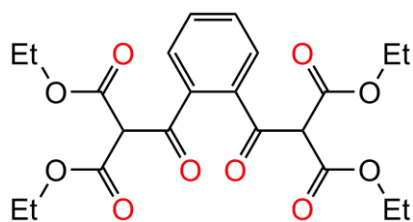
**Figure 14** – The scheme of synthesis of the C-alkylated malonamides. R, R<sub>1</sub> and R<sub>2</sub> are alkyl substituents. Hal stands for a halogen atom (Cl or Br).

Each of the amides **1** – **13** (Fig. 10 – 12) was synthesized in either one or two steps, except for **3** and **10** prepared in three steps, using the commercially available precursors, which is the advantage of these amides.

The attempt to prepare the ester tetraethyl 2,2'-phthaloyldimalonate (Fig. 15) was made with the aim to use it for synthesis of the amide 2,2'-phthaloylbis(*N,N,N',N'*-tetrabutylmalonamide), which would have six carbonyl oxygen donor atoms. Rathke *et al.* reported that diethyl malonate can be acylated with the

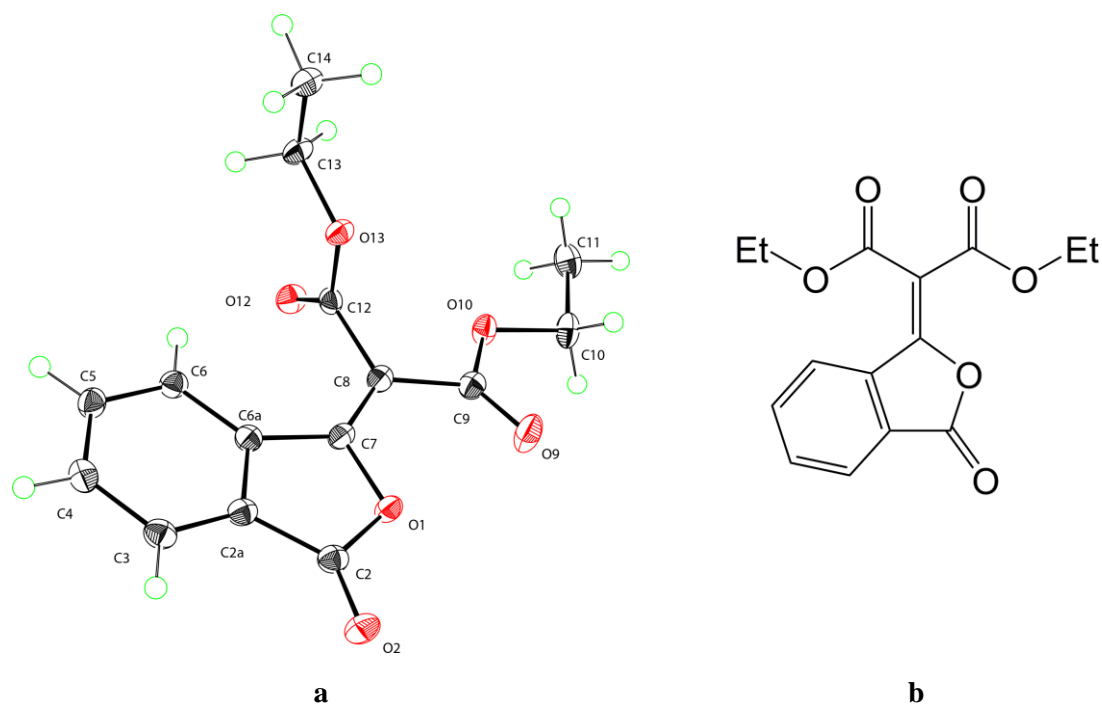
<sup>7</sup> Wahu *et al.* described the synthesis of *N,N,N',N'*-tetraethylmalonamide from diethyl malonate and diethylamine [30]. The reaction was conducted into the sealed vessel, which was irradiated into the microwave oven at 180 °C.

acyl chlorides when treated with a combination of triethylamine and a mild Lewis acid (magnesium chloride) in acetonitrile [100]. Diethyl malonate was reacted with phthaloyl chloride using the synthesis procedure, reported by Rathke *et al.* [100].



**Figure 15** – The molecular structure of tetraethyl 2,2'-phthaloyldimalonate. The carbonyl oxygen atoms are shown in red.

Instead of tetraethyl 2,2'-phthaloyldimalonate (Fig. 15) the organic product, which contained two ethyl groups in different magnetic environments, was obtained in this reaction. Crystals of the compound were examined with single-crystal X-ray diffraction. The product was found to be diethyl 2-(3-oxoisobenzofuran-1(3H)-ylidene)malonate (**14**) (Fig. 16).



**Figure 16** – The molecular structure of diethyl 2-(3-oxoisobenzofuran-1(3H)-ylidene)malonate (**14**), showing the atom-labelling scheme (**a**). Displacement ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are shown in green. The chemical diagram of **14** (**b**).

The formation of **14** can be rationalized by the nucleophilic attack of the oxygen atom, in an enol form, of the keto-diethylmalonate group on the carbon atom of the unreacted acyl chloride group. The mechanism of the formation of **14** was proposed by Naik *et al.*, who obtained this compound by another reaction [114].

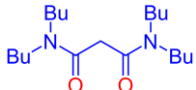
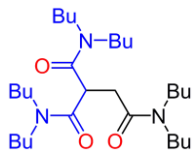
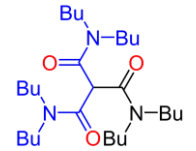
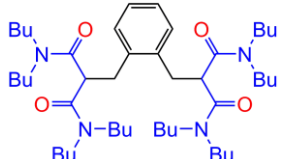
## 6.2 Solvent extraction of Eu(III) with *N,N,N',N'*-tetrabutylmalonamide and its tri- and tetradentate derivatives

Malonamides are the bidentate ligands able to extract trivalent actinides and lanthanides from aqueous solutions with high nitric acid concentrations [19, 55, 56] in contrast to the monodentate ligands such as trialkyl phosphine oxides (TRPO), which extract these elements from moderately concentrated nitric acid solutions [115]. A large work on optimization of a molecular structure of malonamide extractants for trivalent f-block elements has been done [28, 31, 36, 56, 69] and resulted in the development of the DIAMEX process [116].

Lately it has been proposed to use ligands with multiple malonamide groups for extraction of trivalent f-block elements [11, 38, 39]. It was argued that such ligands could extract these elements with higher distribution ratios than conventional bidentate malonamides due to the entropic effect [11, 37].

With an intention to observe and exploit the entropic effect in lanthanide(III) extraction four structurally related amide extractants were synthesized: the bidentate *N,N,N',N'*-tetrabutylmalonamide (**1**) as a reference molecule and its polydentate derivatives, i.e. tridentate ligands **3** and **4** and tetradentate amide **5** (Table 7).

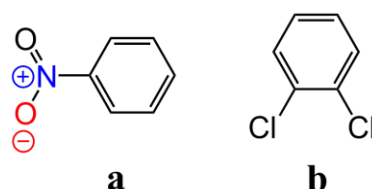
**Table 7** – Molecular structures of the synthesized bidentate *N,N,N',N'*-tetrabutylmalonamide (**1**), shown in blue, and its tri- and tetradentate derivatives. Bu stands for *n*-butyl.

Extractant		Number of oxygen donor atoms
Designation number	Molecular structure	
<b>1</b>		2
<b>3</b>		3
<b>4</b>		3
<b>5</b>		4

The amides **1**, **3** and **5** were found to be soluble in aliphatic kerosene Solvent 70 while the triamide **4** was insoluble in this diluent.

The solutions of the amides **1**, **3** and **5** in Solvent 70 (20 vol. % amide) were pre-equilibrated with the aqueous phase containing 1 M nitric acid and 4 M ammonium nitrate. All of these organic solutions formed a liquid third phase, which is a frequent problem for solvent extraction with malonamides in aliphatic diluents [36, 62, 117].

All four amides **1**, **3**, **4** and **5** were found to be soluble in the aromatic diluents nitrobenzene and 1,2-dichlorobenzene (Fig. 17), and the amide solutions (20 vol. % amide) in these diluents did not form liquid third phases after being pre-equilibrated with the aqueous phase. Therefore further experiments on solvent extraction of europium(III) from the  $^{152}\text{Eu}$  radiotracer aqueous solutions with the synthesized amides were conducted using nitrobenzene and 1,2-dichlorobenzene as diluents of the organic phases.



**Figure 17** – Molecular structures of: **a** – nitrobenzene; **b** – 1,2-dichlorobenzene.

The distribution ratios of Eu(III), determined in the extraction reactions with the amides **1**, **3** – **5** in nitrobenzene and 1,2-dichlorobenzene, are listed in Table 8.

**Table 8** – Distribution ratios of Eu(III) in the extraction reactions with the amides **1**, **3**, **4** and **5**. The aqueous phase: 3 kBq/mL  $^{152}\text{Eu}$ , 0.5 M  $\text{HNO}_3$ , 2.5 M  $\text{NH}_4\text{NO}_3$ . The organic phases: 0.25 M amide in nitrobenzene or 1,2-dichlorobenzene diluents.

Extractant	Distribution ratio of Eu(III) in the organic phase diluent	
	nitrobenzene	1,2-dichlorobenzene
<b>1</b>	$0.163 \pm 0.001$	$0.021 \pm 0.003$
<b>3</b>	$0.123 \pm 0.004$	$0.023 \pm 0.002$
<b>4</b>	$0.044 \pm 0.001$	$0.019 \pm 0.008$
<b>5</b>	$15.4 \pm 0.2$	$1.73 \pm 0.03$
diluent alone	$0.019 \pm 0.005$	$0.017 \pm 0.003$

In nitrobenzene both triamides **3** and **4** have lower abilities to extract europium(III) from the nitrate medium than the bidentate malonamide **1** (Table 8). In contrast the distribution ratio of Eu(III) with the tetraamide **5** was much higher than that with its ‘parent’ diamide **1** (Table 7).

Tetraamide **5** is the bismalonamide ligand bearing two *C*-alkylated *N,N,N',N'*-tetrabutylmalonamide groups onto an *ortho*-xylylene  $\text{C}_6\text{H}_5(\text{CH}_2)_2$  platform. As the platform in a molecule of **5** holds two malonamide groups close together (Table 7), this extracting agent could coordinate to a metal ion with four oxygen atoms, while diamide **1** has only two coordinating oxygens. The plausible tetradentate coordination of **5** with europium(III) in an organic phase could be responsible for the greater distribution ratio.

It was concluded that the increase of the number of amide groups in the ligands alone does not necessarily lead to an increase of the distribution ratios of lanthanides(III) in the extraction experiments. A pronounced effect of a diluent on the extraction of Eu(III) with the amides **1**, **3**, **4** and **5** was observed. The distribution ratios of Eu(III) with all four amides decreased when the diluent in the organic phases was changed from nitrobenzene to 1,2-dichlorobenzene (Table 8). These diluents are both aromatic. However nitrobenzene is more polar than 1,2-dichlorobenzene. Their dipole moments ( $\mu$ ) are equal to

4.02 D and 2.27 D at 25 °C, respectively. Therefore it was concluded that polar diluents favor an extraction of Eu(III) with the studied amides. The effect of a diluent can be associated with more substantial contribution of the charge-separated resonance forms of the amides (Fig. 1) in the media with higher dielectric constants [41, 77].

The use of a radiotracer for the determination of the distribution ratios of Eu(III) in the extraction reactions with the amides **1**, **3**, **4** and **5** (Table 7) required certain precautions to be taken. The extraction experiments with no amide extractants in the organic phase, i.e. with a diluent alone, were performed to make a combined check for the absorption of  $^{152}\text{Eu}$  onto the glass walls of the shaking vials, the extraction of europium(III) by the diluents and the quenching effect [118] of the aromatic diluents. These effects were found to be negligible (Table 8).

The hypothesis that tetraamide **5** was contaminated with a trace of a substance, which is highly able to extract Eu(III), was tested by performing an extraction experiment with macroscopic amounts of Eu(III) in an aqueous phase. The 300  $\mu\text{L}$  aliquots of the organic phase (a 100 mM solution of **5** in nitrobenzene) were contacted separately with the aliquots (300  $\mu\text{L}$ ) of two aqueous phases. Both aqueous phases contained a  $^{152}\text{Eu}$  radiotracer, 0.5 M nitric acid and 2.5 M ammonium nitrate, and one of them was carrier-free, while the other contained a stable europium as a carrier (1 mM  $\text{Eu}(\text{NO}_3)_3$ ). In these two solvent extraction systems the initial Eu(III) concentrations in the aqueous phases were equal to  $1 \cdot 10^{-10}$  M and  $1 \cdot 10^{-3}$  M, respectively, and the corresponding distribution ratios of europium were determined to be  $(3.67 \pm 0.05)$  and  $(3.54 \pm 0.02)$ . These results indicate that the extractant **5** was not contaminated with any impurity extracting europium(III), and the extracted Eu(III) species were predominantly monometallic at the given experimental conditions.

### 6.3 Coordination of the bismalonamides with lanthanide(III) ions

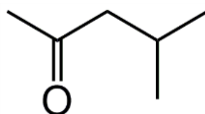
The bismalonamide **5** was found to be particularly efficient at extracting europium(III) from nitric acid solutions among the studied amides (**1**, **3**, **4** and **5**). It was suggested that this ligand could coordinate to a lanthanide(III) ion with four carbonyl oxygen atoms. Such coordination mode promotes favorable entropy changes in the complex formation reactions and therefore might explain an increase in the distribution ratios of Eu(III) in the extraction reactions with **5**. The coordination of the bismalonamides with trivalent lanthanide ions was investigated both in solutions and in the solid-state complexes.

#### 6.3.1 Stoichiometry of the lanthanide(III) complexes with tetraamide **5** formed during solvent extraction

The lanthanide(III) – tetraamide **5** stoichiometric ratios in the extracted species were determined by the slope analysis [7]. In this method, described in detail in the theory section, the plot of distribution ratios of a metal ion as a function of an extractant concentration in an organic phase is constructed in the logarithmic scale [7, 56, 119]. Typically it is assumed that the activity coefficient of an extractant is constant within the selected range of its concentrations [48]. Under ideal conditions the resulting plot is a straight line with a slope, the value of which is equal to a metal – extractant stoichiometric ratio in the extracted complexes [7].

The composition of the extracted species often depends on a diluent of an organic phase and a medium of an aqueous phase [7]. Therefore the stoichiometry of the lanthanide(III) complexes with tetraamide **5** in the extraction reactions was studied using different diluents of the organic phases and counter-ions in the aqueous phases.

Nitrobenzene, Solvesso 150 ND and methyl isobutyl ketone (MIBK) (Fig. 18) were selected as the diluents of the organic phases. When the solutions of **5** with these three diluents were contacted with the aqueous phases, no formation of a liquid third layer or solid was observed.



**Figure 18** – Molecular structure of methyl isobutyl ketone (MIBK).

Nitrobenzene and Solvesso 150 ND are the polar and non-polar aromatic diluents, respectively, while MIBK is the polar non-aromatic one.

The nitrate and perchlorate anions, selected as the counter-ions of the aqueous phases, have different ability to coordinate with lanthanides(III). Perchlorates ( $\text{ClO}_4^-$ ) are generally considered to be weakly coordinating anions [23, 120]. In contrast nitrates are known to form both inner- and outer-sphere coordination complexes with lanthanide(III) ions [7, 121, 122]. Moreover nitrates can act as either mono- ( $\kappa^1\text{O-NO}_3$ ) or bidentate ( $\kappa^2\text{O-NO}_3$ ) ligands in the inner-sphere coordination complexes with lanthanides(III) [123].

#### 6.3.1.1 Stoichiometry of the Eu(III) and $\text{HNO}_3$ complexes extracted from nitrate media into nitrobenzene

The equilibrium between the aqueous and organic phases in the reactions of Eu(III) extraction with **5** from nitrate media into nitrobenzene was achieved within 30 minutes of agitation (Table 9).

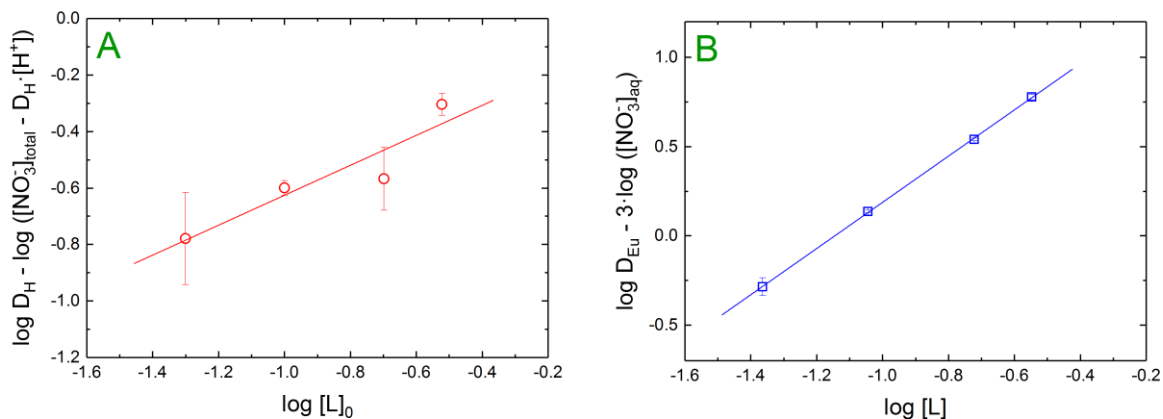
**Table 9** – The effect of the phase contact time on distribution ratios of Eu(III). Aq. phase: 0.9 kBq/mL  $^{152}\text{Eu}$ , 0.13 M  $\text{HNO}_3$ , 0.6 M  $\text{NH}_4\text{NO}_3$ . Org. phase: 0.25 M tetraamide **5** in nitrobenzene.

Phase contact time, min	$D_{\text{Eu(III)}}$
30	$1.74 \pm 0.03$
60	$1.74 \pm 0.04$
120	$1.73 \pm 0.03$

In all further extraction experiments with the solutions of **5** in nitrobenzene the aqueous and organic phases were agitated for 30 min to reach the equilibria.

The total concentration of nitrate ions before and after the extraction reactions was kept close to a constant value by using the aqueous phases with relatively high ammonium nitrate concentration, i.e. 0.6 M  $\text{NH}_4\text{NO}_3$  vs 0.13 M  $\text{HNO}_3$ .

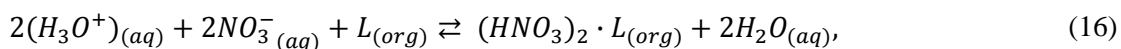
It was demonstrated that tetraamide **5** extracts nitric acid from aqueous solutions into nitrobenzene (Fig. 19). The change in the total nitrate concentration ( $[\text{NO}_3^-]_{\text{total}}$ ) in the aqueous phases due to the extraction of nitric acid was insignificant, i.e. the 4 % decrease in  $[\text{NO}_3^-]_{\text{total}}$  was calculated at the maximum extraction of  $\text{HNO}_3$  (Fig. 19). Therefore the eqn. (8) is valid for the stoichiometry determination in the reaction of nitric acid extraction with **5**.



**Figure 19** – The slope analysis of the  $HNO_3$  (A) and  $Eu(III)$  (B) extraction reactions.

**A** – The dependence of  $(\log D_H - \log ([NO_3^-]_{total} - D_H \times [H^+]))$  on  $\log [L]_0$ ; **B** – the dependence of  $(\log D_{Eu} - 3 \times \log ([NO_3^-]_{aq}))$  on  $\log [L]$ , where  $[L]_0$  and  $[L]$  are the initial and free (i.e. corrected to the  $HNO_3$  extraction) concentrations of the extractant in the org. phases, respectively. Org. phases: (0.05 – 0.30) M tetraamide **5** in nitrobenzene. The aq. phases: 0.13 M  $HNO_3$ , 0.6 M  $NH_4NO_3$ . The aq. phases (B) contain 0.9 kBq/mL  $^{152}Eu$ . The solid lines are the linear regressions with the slopes  $(0.53 \pm 0.15)$  (A) and  $(1.29 \pm 0.01)$  (B). The uncertainty bars are at  $\pm 2\sigma$ .

The empirical stoichiometric coefficient in this reaction was found to be  $n = (0.53 \pm 0.15)$ , which means that one  $H^+$  cation is coordinated with a half of the molecule of **5** in the extracted species. This empirical ratio can be interpreted by the formation of predominantly  $(HNO_3)_2 \cdot L$  species in an organic phase according to the reaction equation:



where  $L$  stands for a molecule of **5**. In this case two  $N,N,N',N'$ -tetrabutylmalonamide ligating groups of **5** (Table 7) most likely operate independently of each other in the reaction of nitric acid extraction, being each coordinated with one  $H^+$  cation.

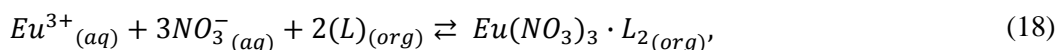
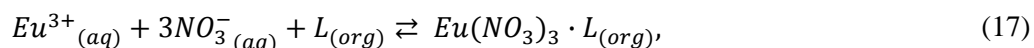
The apparent equilibrium constant  $K_{2,1}$  of the reaction (16) and its uncertainty were calculated using eqns. (6) and (7) and the formulae for a propagation of random errors [18]:  $\log K_{2,1} = (0.44 \pm 0.16)$ , where the subscript (2,1) indicates the numbers of  $H^+$  ions and the extractant molecules in the extracted species, respectively.

The interpretation of the stoichiometry of the reaction (16) is consistent with the reported experimental data on extraction of nitric acid by conventional bidentate malonamides [19, 55, 58, 59, 77, 78, 124, 125]. Musikas *et al.* studied nitric acid extraction with  $N,N'$ -dimethyl- $N,N'$ -dioctylmalonamide (DMDOMA) into *tert*-butylbenzene and determined the formation of the species  $HNO_3 \cdot L_2$ ,  $HNO_3 \cdot L$  and  $(HNO_3)_2 \cdot L$  (where  $L$  is a molecule of DMDOMA) in the organic phases by the slope analysis with the respective extraction constants (in the molar scale) at  $[HNO_3]_{(aq)} < 5$  M:  $\log K_{1,2} = -0.19$ ,  $\log K_{1,1} = -0.96$ , and  $\log K_{2,1} = -2.12$  [124]. Four adducts  $HNO_3 \cdot L_2$ ,  $HNO_3 \cdot L$ ,  $(HNO_3)_2 \cdot L$  and  $(HNO_3)_3 \cdot L$ , where  $L$  is a molecule of  $N,N'$ -dimethyl- $N,N'$ -dibutyltetradecylmalonamide (DMDBTDMA), were identified by Nigond *et al.* as the extracted species in the reactions of nitric acid extraction with DMDBTDMA into TPH [125]. The respective extraction constants (in the molar scale for 0.72 M DMDBTDMA) were found to be:  $\log K_{1,2} = -0.61$ ,  $\log K_{1,1} = -0.70$ ,  $\log K_{2,1} = -2.56$ , and  $\log K_{3,1} = -5.09$  [125]. Tian *et al.* studied nitric acid extraction with  $N,N'$ -diethyl- $N,N'$ -dibutylmalonamide (DEDBMA) into a mixture of dodecane (80 %) and xylene (20 %) [78]. The composition of the extracted complexes depended on the acidity of an aqueous phase, and the formation



of the species  $\text{HNO}_3 \cdot \text{L}_2$  at  $[\text{HNO}_3]_{(\text{aq})} < 1.5 \text{ M}$ ,  $\text{HNO}_3 \cdot \text{L}$  at  $(1.5 - 3) \text{ M HNO}_3$ , and  $(\text{HL}^+) \cdot (\text{NO}_3^-) \cdot (\text{HNO}_3)$ , or  $(\text{HNO}_3)_2 \cdot \text{L}$ , at  $[\text{HNO}_3]_{(\text{aq})} > 3 \text{ M}$  (where L is a molecule of DEDBMA) was determined by the slope analysis [78]. The crystal structure  $[\text{H}^+ \cdot \text{DMDCHMA}]_2 \cdot [\text{CoCl}_4]^{2-}$ , where DMDCHMA is *N,N'*-dimethyl-*N,N'*-dicyclohexylmalonamide, was obtained by Chan *et al.* [58]. The cations of this structure, having the 1:1 stoichiometric ratio of  $\text{H}^+$  and the bidentate malonamide, can be viewed as the solid-state analogues of the nitric acid species  $\text{HNO}_3 \cdot \text{L}$  extracted with the malonamides (L) and determined by the slope analysis [19, 78, 124, 125].

The stoichiometry of the Eu(III) extraction reaction with tetraamide **5** from nitrate media into nitrobenzene was studied (Fig. 19). In this experiment distribution ratios of nitric acid were not being measured. However the reaction of the acid extraction was taken into account when calculating the ‘free extractant’ concentration [7] in the organic phases. The molecules of **5** are termed ‘free extractant’ if not being bonded to neither Eu(III) nor  $\text{H}^+$  ions. The empirical stoichiometric coefficient, calculated from the eqn. (8), was found to be  $n = (1.29 \pm 0.01)$ . The fractional value of the coefficient can be explained by the change of activity coefficients of the extractant in the organic phases [7]. Alternatively it can be assumed that two Eu(III) species are being formed in the organic phases according to the extraction reactions:



where L stands for a molecule of **5**.

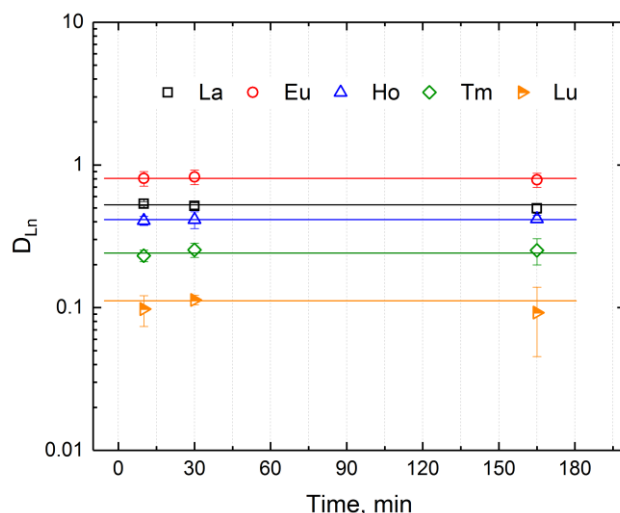
Each of the reactions (17) and (18) can be described by the apparent equilibrium constants  $K_{1,1}$  and  $K_{1,2}$ , respectively, using eqn. (6). Then the distribution ratio of Eu(III) can be expressed by the equation:

$$D_{\text{Eu}} = \frac{K_{1,1} \times [\text{NO}_3^-]_{(\text{aq})}^3 \times [\text{L}]_{(\text{org})} + K_{1,2} \times [\text{NO}_3^-]_{(\text{aq})}^3 \times [\text{L}]_{(\text{org})}^2}{1 + \beta_1 \times [\text{NO}_3^-]_{(\text{aq})} + \beta_2 \times [\text{NO}_3^-]_{(\text{aq})}^2}, \quad (19)$$

where  $\beta_1$  and  $\beta_2$  are the overall stability constants of the  $[\text{EuNO}_3]^{2+}$  and  $[\text{Eu}(\text{NO}_3)_2]^+$  complexes in the aqueous phases. The nitrate complexes of lanthanides(III) in aqueous solutions are weak and barely depend on the ionic strength [22, 126]. Therefore the overall stability constants  $\beta_1 = (1.86 \pm 0.04)$  and  $\beta_2 = (0.43 \pm 0.02)$  of the respective  $[\text{EuNO}_3]^{2+}$  and  $[\text{Eu}(\text{NO}_3)_2]^+$  complexes, determined by Andersson *et al.* in the aqueous solutions with the ionic strength  $I = 5 \text{ M}$  [22], were used to calculate the Eu(III) extraction constants  $K_{1,1}$  and  $K_{1,2}$  despite the ionic strength of the aqueous phases in these reactions was  $I = 0.73 \text{ M}$ . The observed equilibrium constants  $K_{1,1}$  and  $K_{1,2}$  of the reactions (17) and (18), calculated from the eqn. (19), are equal:  $\log K_{1,1} = (1.24 \pm 0.02)$  and  $\log K_{1,2} = (1.59 \pm 0.06)$ . In the section 4 it was pointed out that there is no universally accepted view on the stoichiometry of the reactions of lanthanide(III) extraction with the conventional bidentate malonamides from nitrate media. The stoichiometric ratios of lanthanides(III) and malonamides in the extracted species, determined by the slope analysis, have been reported to be 1:2 (e.g. [76]), 1:3 (e.g. [61]) and 1:4 (e.g. [56]). Also the extracted species, having the 1:1 and 1:2 ratios, were determined by the method of an organic phase saturation by extraction [127, 128]. Nevertheless the assumption that two Eu(III) species  $\text{Eu}(\text{NO}_3)_3 \cdot \text{L}_{(\text{org})}$  and  $\text{Eu}(\text{NO}_3)_3 \cdot \text{L}_2_{(\text{org})}$  are being formed in the organic phases during extraction is consistent with these literature data considering the fact, that a molecule of tetraamide **5** (L) contains two *N,N,N',N'*-tetrabutylmalonamide ligating groups (Table 7).

### 6.3.1.2 Stoichiometry of the lanthanide(III) complexes extracted from nitrate media into kerosene

The stoichiometry of the reactions of lanthanide(III) extraction with tetraamide **5** from nitrate media into the aromatic kerosene Solvesso 150 ND was studied. In these experiments no formation of a liquid third phase was observed upon the pre-equilibration of the organic phases with the nitric acid solutions. In general adducts of nitric acid and conventional bidentate malonamides have higher solubility in aromatic diluents than in aliphatic ones [62, 128]. It is worth to mention that Solvesso 150 has been used as the diluent of the organic phase in the uranium extraction with TBP in the CHEMEX process [129].

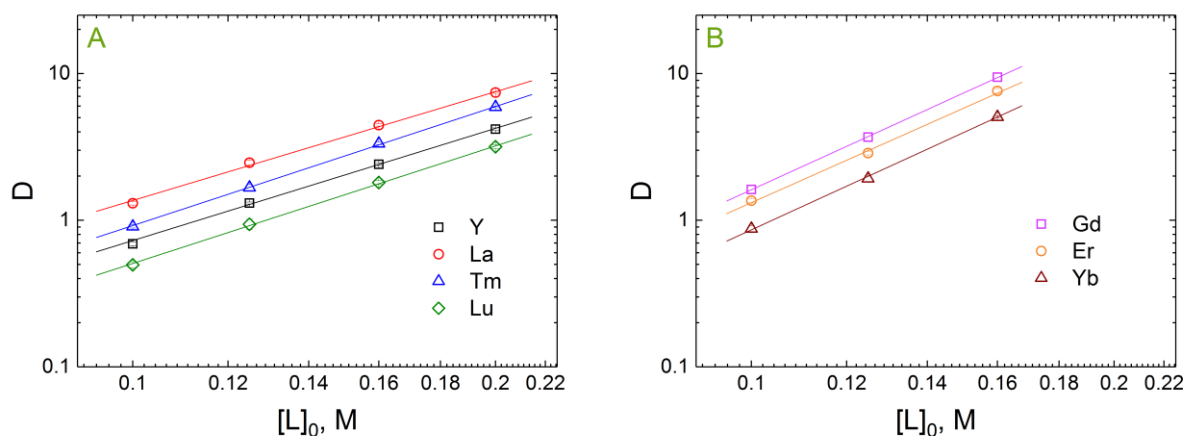


**Figure 20** – The dependencies of the distribution ratios of the lanthanides(III) on the phase contact time. The aq. phase:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; 4 M  $HNO_3$ . The org. phase: 0.18 M tetraamide **5** in Solvesso 150 ND, 10 vol. % 1-decanol. The solid lines are the linear regressions with the slopes = 0. The uncertainty bars are at  $\pm 1\sigma$ .

The equilibrium between the aqueous and organic phases in the reactions of lanthanide(III) extraction with **5** from nitrate media into Solvesso 150 ND, modified with 10 vol. % 1-decanol, is achieved within ten minutes of agitation (Fig. 20). The modifier (1-decanol) was added to the organic phase to improve the separation of the aqueous and organic phases. In all further extraction experiments with the solutions of **5** in Solvesso 150 ND the aqueous and organic phases were contacted for 10 min to reach the equilibria.

The empirical stoichiometric coefficients in the reactions of lanthanide(III) and yttrium(III) extraction were determined by the slope analysis (Fig. 21). The total concentration of nitrate ions before and after extraction was kept close to a constant value by the pre-equilibration of the organic phases with the respective nitric acid solution. The coefficients are listed in Table 10.

In the reactions of extraction of Y, La – Nd, Sm, Tb, Ho, Tm, and Lu the dependencies of  $\log D$  on  $\log [L]_0$ , where  $[L]_0$  is an initial concentration of the extractant in an organic phase, were the straight lines (Fig. 21 A) with the slopes  $n = (2.14 - 2.70)$  (Table 10) for  $[L]_0 = (0.10 - 0.20)$  M. In the reactions of Eu, Gd, Dy, Er and Yb extraction these dependencies were also straight lines (Fig. 21 B) for  $[L]_0 = (0.10 - 0.16)$  M, however the slopes of the regression lines had larger values  $n = (3.36 - 4.01)$  (Table 10). At further increase of tetraamide **5** concentration in the organic phase to 0.20 M the dependencies in these reactions became non-linear.



**Figure 21** – The dependencies of  $\log D$  on  $\log [L]_0$  in the reactions of extraction of: **A** – Y, La, Tm, and Lu; **B** – Gd, Er, and Yb.  $[L]_0$  is an initial concentration of the extractant in an org. phase. The aq. phase:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; 5 M  $\text{HNO}_3$ . The organic phases:  $(0.10 - 0.20)$  M tetraamide **5** in Solvesso 150 ND. The solid lines are the linear regressions with the slopes: **A** –  $n = (2.46 - 2.70)$ ; **B** –  $n = (3.66 - 3.77)$ . The uncertainty bars are at  $\pm 1\sigma$ .

**Table 10** – The empirical stoichiometric coefficients ( $n$ ) in the reactions of lanthanide(III) and Y(III) extraction with tetraamide **5** into Solvesso 150 ND determined by the slope analysis. The aq. phase:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; 5 M  $\text{HNO}_3$ . The org. phases:  $(0.10 - 0.20)$  M tetraamide **5** in Solvesso 150 ND.

Element	Atomic number	Slope ( $n$ )	Uncertainties at $\pm 1\sigma$
Y	39	2.54	0.07
La	57	2.46	0.08
Ce	58	2.68	0.03
Pr	59	2.25	0.12
Nd	60	2.14	0.10
Sm	62	2.28	0.06
Eu	63	3.36	0.10
Gd	64	3.75	0.04
Tb	65	2.32	0.06
Dy	66	4.01	0.25
Ho	67	2.60	0.02
Er	68	3.66	0.21
Tm	69	2.70	0.04
Yb	70	3.77	0.08
Lu	71	2.66	0.05

The empirical stoichiometric coefficients in the reactions of lanthanide(III) extraction with conventional bidentate malonamides, determined by the slope analysis, may fluctuate across the lanthanide series, which has been demonstrated by several researchers e.g. [55, 77, 79]. It was assumed that these fluctuations are due to either non-ideality of solutions of the amide extractants in organic diluents [77, 79], or the extractant aggregation phenomena [128], or the outer sphere coordination of the extracted complexes with the amides [56, 128].

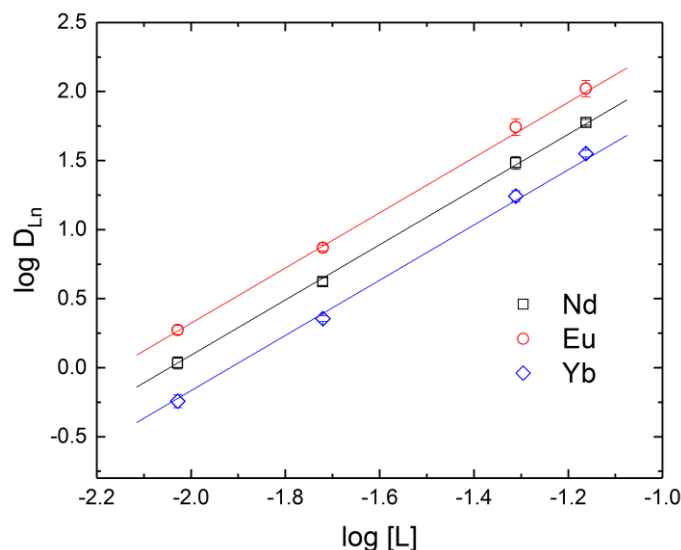
### 6.3.1.3 Stoichiometry of the lanthanide(III) complexes extracted from perchlorate media into methyl isobutyl ketone

The stoichiometry of the reactions of lanthanide(III) extraction with tetraamide **5** from perchlorate media into methyl isobutyl ketone (MIBK) was studied. MIBK, also known as hexone, is the polar non-aromatic diluent (Fig. 18), which has been used as both the extractant and the diluent of the organic phase in the first solvent extraction process (the REDOX) for large-scale separation of uranium and plutonium from irradiated nuclear fuel in the United States [116].

In the current experiments the total concentration of perchlorates before and after the lanthanide(III) extraction reactions was kept close to a constant value by the pre-equilibration of the organic phases with the respective perchlorate solution as well as by using the aqueous phases with small Ln(III) concentrations.

The tests indicated that the pure diluent MIBK does not extract lanthanide(III) ions from perchlorate solutions, and the equilibrium in these extraction reactions is achieved within 30 min of agitation of the phases.

The empirical stoichiometric coefficients in the reactions of lanthanide(III) extraction with **5** from perchlorate media into MIBK were determined by the slope analysis (Fig. 22). The stoichiometric coefficients, calculated from the eqn. (9), are listed in Table 11.

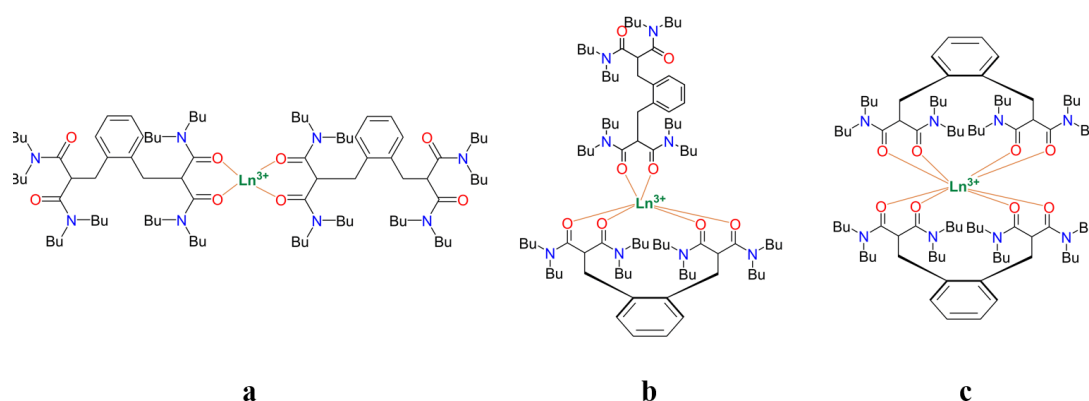


**Figure 22** – The dependencies of  $\log D$  on  $\log [L]$  in the reactions of extraction of Nd, Eu, and Yb.  $[L]$  is a concentration of the extractant in an org. phase, corrected to the extraction of  $\text{Ln}(\text{ClO}_4)_3 \cdot \text{L}_{2(\text{org})}$  species. The org. phases: (0.01 – 0.07) M tetraamide **5** in MIBK. The aq. phase: (0.100 ± 0.002) mM each element La, Nd, Eu, Dy, Er, and Yb; 0.1 M  $\text{HClO}_4$ ; 3 M  $\text{NaClO}_4$ . The solid lines are the linear regressions with the slopes = 2. The uncertainty bars are at ± 2σ.

**Table 11** – The empirical stoichiometric coefficients ( $n$ ) in the reactions of lanthanide(III) extraction with tetraamide **5** from perchlorate media into MIBK determined by the slope analysis. The org. phases: (0.01 – 0.07) M tetraamide **5** in MIBK. The aq. phase: (0.100 ± 0.002) mM each element La, Nd, Eu, Dy, Er, and Yb; 0.1 M HClO<sub>4</sub>; 3 M NaClO<sub>4</sub>. The values in parentheses are the uncertainties at ± 2σ.

Stoichiometric coefficient ( $n$ ) in a reaction of lanthanide(III) extraction					
La	Nd	Eu	Dy	Er	Yb
1.91 (0.02)	2.03 (0.03)	2.04 (0.05)	2.05 (0.05)	2.08 (0.03)	2.10 (0.03)

In summary it was determined by the slope analysis that the lanthanide complexes with tetraamide **5**, formed during the reactions of lanthanide(III) extraction from nitrate or perchlorate media into nitrobenzene, kerosene or MIBK, have the following stoichiometric ratios of a metal and the extractant: (1:1) and (1:2) (nitrate media / nitrobenzene); (1:2), (1:3) and (1:4) (nitrate media / kerosene); (1:2) (perchlorate media / MIBK). Since a molecule of tetraamide **5** contains two *N,N,N',N'*-tetrabutylmalonamide functional groups with four oxygen donor atoms in total (Table 7), in the extracted complexes the tetraamide might coordinate with lanthanide ions by different modes, for instance as schematically depicted in Fig. 23 for the extracted complexes with the (1:2) stoichiometry.



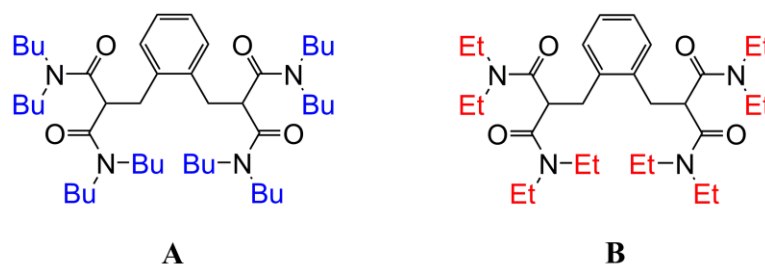
**Figure 23** – Chemical diagrams of the hypothetical extracted species **a**, **b** and **c**, showing possible coordination of two molecules of tetraamide **5** with one lanthanide(III) ion. The species **a**, **b** and **c** have the (1:2), (1:3) and (1:4) ratios of a lanthanide and the bidentate malonamide ligating groups of tetraamide **5**, respectively. Counter-ions are omitted.

The coordination modes cannot be established from the slope analysis data. Single-crystal X-ray diffraction was used to investigate the coordination of lanthanide(III) ions with the tetraamide ligands.

### 6.3.2 Single-crystal structures of the bismalonamide complexes with lanthanides(III)

The bismalonamide **8** was synthesized and used as the ligand for growing single-crystal complexes with lanthanide(III) ions, because **8** and the extractant **5** are the homologous bismalonamides, i.e. their molecular structures differ only by the size of *N*-alkyl substituents of the amide groups (Fig. 24).

The bismalonamide **8** was reacted with every member of the lanthanide series, excluding radioactive promethium, in nitrate media in acetonitrile. However single crystals, suitable for a structure determination, were obtained for the neodymium and cerium complexes only. No attempt was made to prepare single crystal complexes of **8** with the whole lanthanide series in perchlorate media, and only the neodymium(III) perchlorate complex with **8** was obtained.

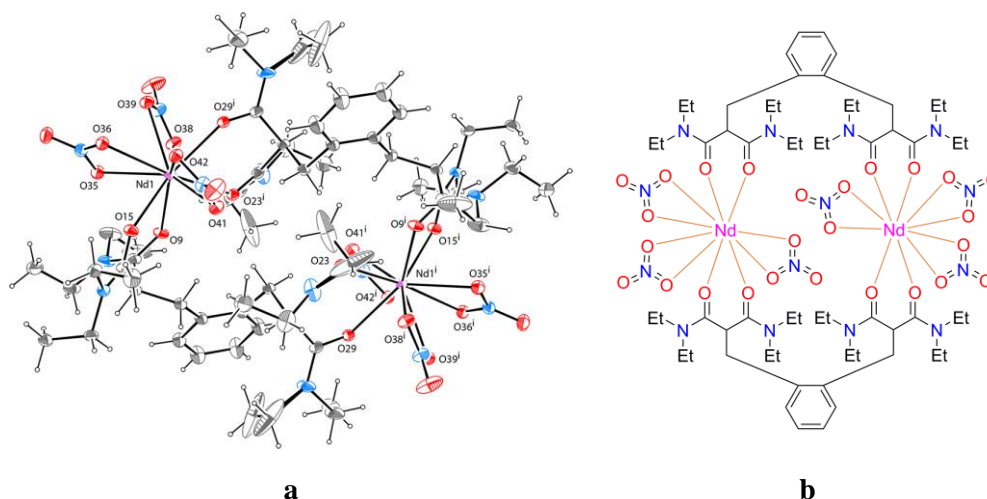


**Figure 24** – Molecular structures of the homologous bismalonamides:  
**a** – 2,2'-(1,2-phenylenebis(methylene))bis(*N,N,N',N'*-tetrabutylmalonamide) (**5**);  
**b** – 2,2'-(1,2-phenylenebis(methylene))bis(*N,N,N',N'*-tetraethylmalonamide) (**8**).  
*Bu* and *Et* stand for *n*-butyl ( $n\text{-C}_4\text{H}_9$ ) and ethyl ( $\text{C}_2\text{H}_5$ ), respectively.

For convenience the bismalonamide **8** is denoted as 'L' in the structural formulae of the synthesized crystal complexes. The coordination geometry of the lanthanides(III) in the obtained structures was investigated with single-crystal X-ray diffraction.

*[Nd<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>L<sub>2</sub>]·(CH<sub>3</sub>CN)<sub>3</sub> (**15**)*

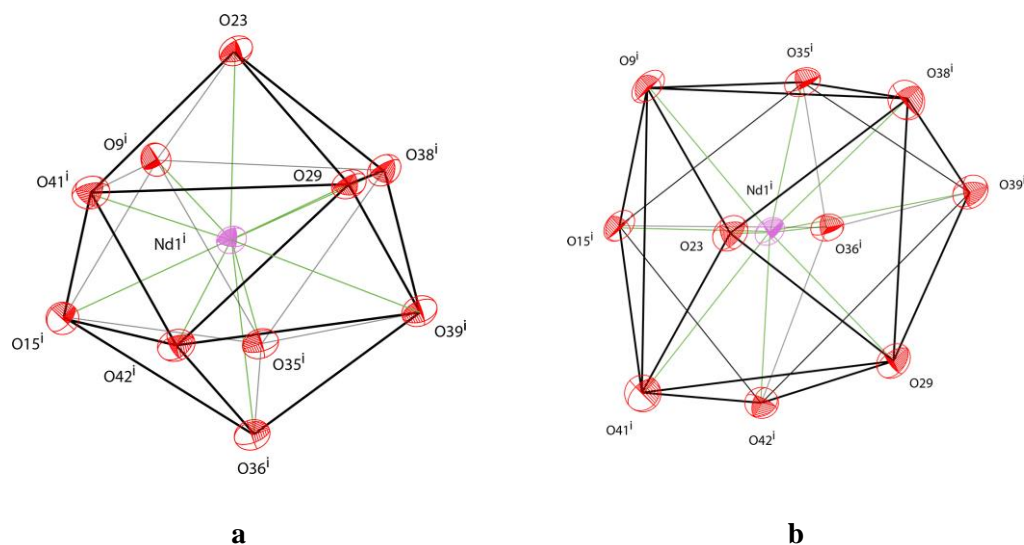
The compound **15** is composed of the dimeric species Nd<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>L<sub>2</sub> and three molecules of acetonitrile (the solvent), trapped in cavities in the crystal. There are two crystallographically equivalent neodymium atoms in the dimer Nd<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>L<sub>2</sub>. Each of these is ten coordinate and bonded to three bidentate nitrate anions ( $\kappa^2\text{-O-NO}_3$ ) and two bidentate *N,N,N',N'*-tetraethylmalonamide (TEMA) units from two different molecules of the ligand L (Fig. 25). This coordination number, as well as the location of the nitrate anions in the inner coordination sphere of the metal, is typical for the nitrato complexes of lanthanides(III) with conventional bidentate malonamides e.g. [25, 66]. Moreover in all six reported crystal structures of the neodymium(III) nitrato complexes with bidentate malonamides (CSD, 2018) the metal ion is ten coordinate and nitrates are bidentate and inner-sphere coordinate [25, 58, 66, 67].



**Figure 25** – The structure of *[Nd<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>L<sub>2</sub>]·(CH<sub>3</sub>CN)<sub>3</sub> (**15**): **a** – ORTEP drawing (30% probability ellipsoids); carbon – gray, oxygen – red, nitrogen – blue, hydrogen – white; molecules of solvent (CH<sub>3</sub>CN) have been omitted for clarity; **b** – chemical diagram of **15**.*

The coordination polyhedron of Nd in the structure **15** is a distorted bicapped square antiprism (Fig. 26). It has been shown that the analogous polyhedra of neodymium(III) in the nitrato complexes with bidentate malonamides exist in three isomeric forms: **A**, **B** or **D** (Fig. 7 and Table 2). The isomeric form

of the Nd polyhedron in **15** is **B**, which previously has been observed only in the nitrate complexes of lanthanides(III) with *N,N,N',N'*-tetramethylmalonamide (TMMA) (Table 2).



**Figure 26** – The coordination polyhedron of the  $\text{Nd}^{3+}$  ion in **15** (bicapped square antiprism): **a** – side view; **b** – top view.

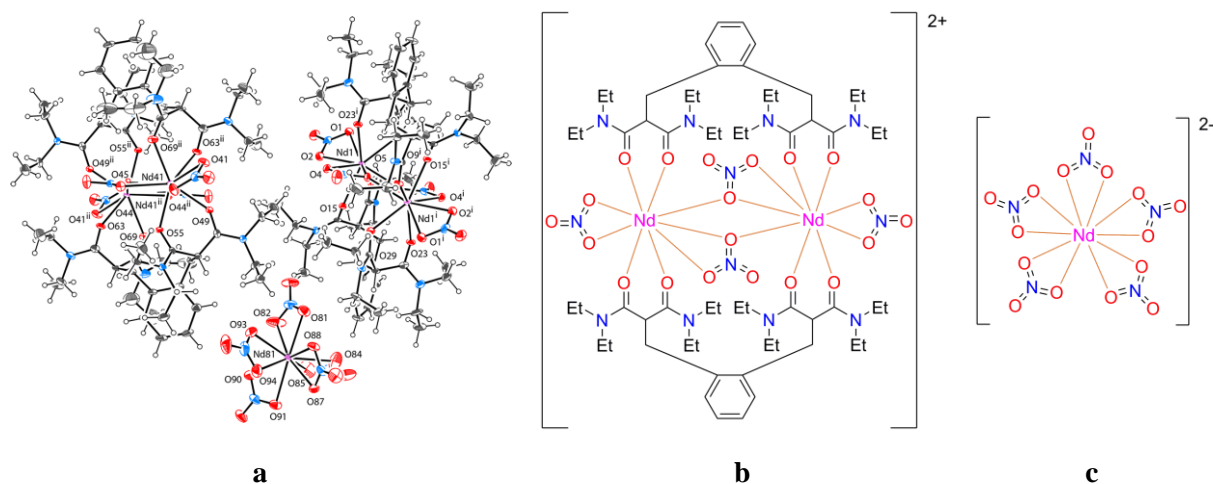
The bond distances between neodymium(III) ion and its coordination environment are similar to the corresponding distances in the nitrate complexes of Nd(III) with conventional bidentate malonamides reported in the literature [25, 58, 66, 67].

The unique feature of structure **15**, which clearly distinguishes it from all known crystalline nitrate complexes of lanthanide(III) ions with malonamides, is the binuclear coordination of the ligand **8** with neodymium(III). The distance between two Nd atoms in the dimeric complex is 8.467 Å. Moreover, the binuclear species  $\text{Nd}_2(\text{NO}_3)_6\text{L}_2$  in **15** is a macroheterocycle rather than a bridge-type structure such as the binuclear complexes of lanthanide(III) nitrates with succinamides [53]. The metal-to-ligand stoichiometry in the structure **15** is 2:2 (or 1:1 when the empirical ratio of Nd:L is considered).



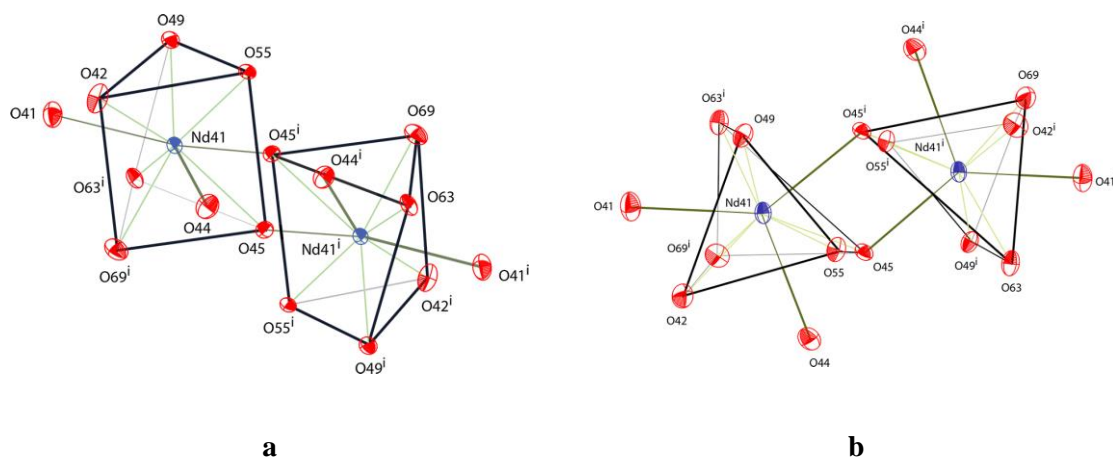
The structure **16** consists of two crystallographically independent halves of the cationic complex  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$ , the anionic complex  $[\text{Nd}(\text{NO}_3)_5]^{2-}$  and molecules of acetonitrile (the solvent), trapped in cavities in the crystal. The cations are the centrosymmetric dimeric species  $\text{Nd}_2(\text{NO}_3)_4\text{L}_2$  that contain two crystallographically equivalent neodymium(III) atoms and two bismalonamide **8** ligands (Fig. 27). Each of the Nd atoms in the complex cation is nine coordinate and bonded with two bidentate *N,N,N',N'*-tetraethylmalonamide units from two different molecules of the ligand, one bidentate nitrate ( $\kappa^2\text{O}-\text{NO}_3$ ), one monodentate and one bidentate bridging nitrates ( $\mu-\kappa^1\text{O}-\kappa^2\text{O}, \text{O}'-\text{NO}_3$ ). These two bridging nitrates connect two neodymium atoms in the cation  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$  through two Nd-O(nitrate)-Nd bridges. Such bridges are rare for the nitrate complexes of lanthanides [130].





**Figure 27** – The structure of  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2] \cdot [\text{Nd}(\text{NO}_3)_5] \cdot (\text{CH}_3\text{CN})_{1.5}$  (**16**): **a** – ORTEP drawing (30% probability ellipsoids); carbon – gray, oxygen – red, hydrogen – white; molecules of solvent ( $\text{CH}_3\text{CN}$ ) have been omitted for clarity; **b**, **c** – chemical diagrams of the cation  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$  and the anion  $[\text{Nd}(\text{NO}_3)_5]^{2-}$  of **16**, respectively.

The coordination polyhedra of the neodymium(III) ions in the complex cation can be described as distorted tricapped trigonal prisms (Fig. 28) typical for hydrated lanthanide(III) ions [92].



**Figure 28** – The coordination polyhedra of  $\text{Nd}^{3+}$  ions in the cation  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$  of **16** (tricapped trigonal prisms bridged by  $\text{O}45$  and  $\text{O}45^i$  oxygen atoms): **a** – side view; **b** – top view.

The complex anion  $[\text{Nd}(\text{NO}_3)_5]^{2-}$  consists of a ten coordinate central neodymium ion bonded with five bidentate nitrates. Its coordination polyhedron is a distorted bicapped square antiprism.

The bond distances of neodymium(III) ions in the cation  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$  (mean value 2.483(8) Å) and anion  $[\text{Nd}(\text{NO}_3)_5]^{2-}$  (mean value 2.51(1) Å) in the structure **16** are different due to the difference in the coordination environment of these metal ions. The distances between two Nd atoms in the crystallographically independent halves of the cationic complex  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$  are equal to 4.388 Å and 4.394 Å, being approximately twice as short as those in structure **15**.

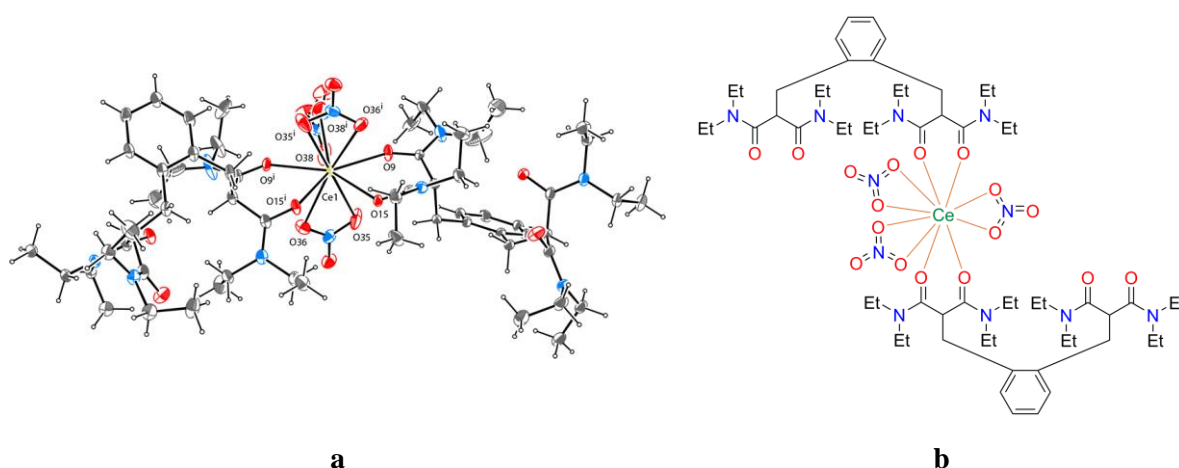
The metal-to-ligand stoichiometry in the structure **16** is 3:2, however it is equal to 2:2 in the cation  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2]^{2+}$ , as in structure **15**.



In the studies of the lanthanide single-molecule magnets binuclear lanthanide(III) complexes play an important role [131]. The lanthanide(III) complexes, isostructural to the binuclear neodymium(III) ones **15** and **16**, may be of interest for this area of research.

#### $Ce(NO_3)_3 \cdot L_2$ (**17**)

The structure **17** is composed of a cerium(III) cation, two bismalonamide **8** ligands and three nitrate anions. The cerium(III) ion is ten coordinate. It is surrounded by two chelating bidentate malonamide units from two bismalonamide ligands and three bidentate nitrates ( $\kappa^2 O-NO_3$ ) (Fig. 29). The nitrates are located in the inner coordination sphere of cerium, as in the structures **15** and **16**. One nitrate is disordered over two positions.



**Figure 29** – The structure of  $Ce(NO_3)_3 \cdot L_2$  (**17**): **a** – ORTEP drawing (30% probability ellipsoids); carbon – gray, oxygen – red, nitrogen – blue, hydrogen – white; **b** – chemical diagram of **17**.

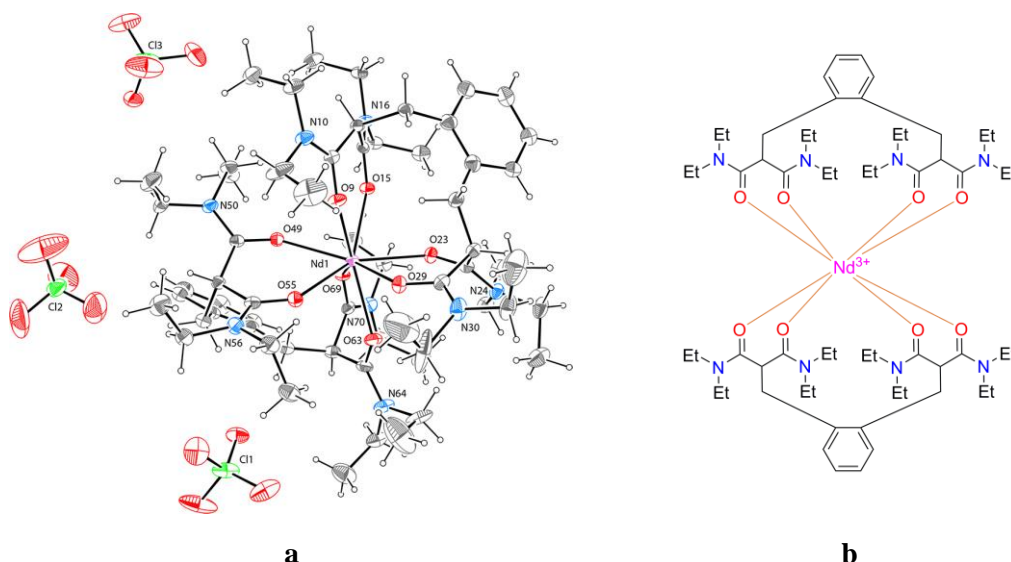
The coordination polyhedron of Ce is a distorted bicapped square antiprism. The isomeric form of the polyhedron is **A** (Fig. 7).

There is a  $C_2$  rotational symmetry in the structure **17**. The  $C_2$  axis passes through the cerium atom and the average of the two locations of the disordered nitrate's nitrogen atom (Fig. 29).

The mean value of the  $Ce^{3+} - O$  bond distances in **17** (2.57(1) Å) is larger than that in the neodymium(III) complex **15** (2.54(1) Å), which can be reconciled by the difference in the ionic radii of the two ions [132]. The structure **17** has the 1:2 metal-to-ligand stoichiometry. Despite the quality of the crystallographic data for the structure **17** is lower than desired this species is important. This structure illustrates that it is possible to open the macrocycle in **15** by bonding a single metal atom only to half of the amide oxygen atoms present in a molecule of the bismalonamide **8**.

#### $[NdL_2] \cdot (ClO_4)_3 \cdot C_2H_5OH$ (**18**)

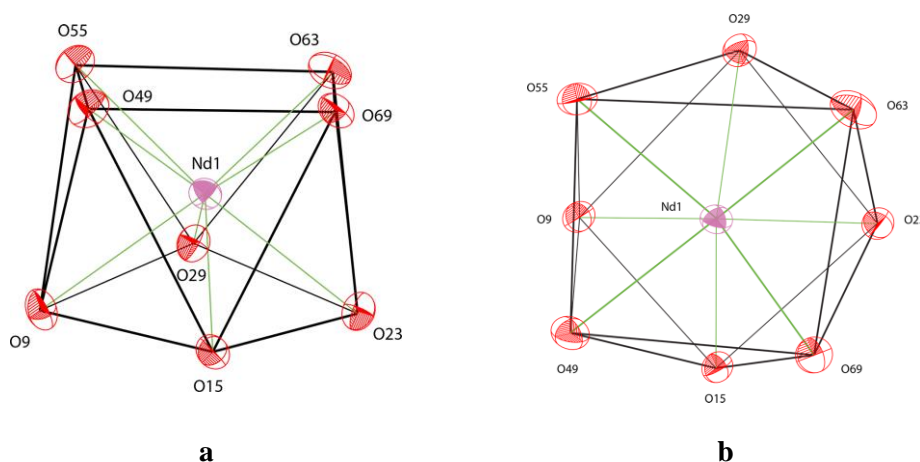
The compound **18** is the complex of neodymium(III) perchlorate with bismalonamide **8**. It consists of one large complex cation  $[NdL_2]^{3+}$ , three perchlorate anions  $ClO_4^-$  and one molecule of ethanol (the solvent) trapped in cavities in the crystal. The Nd(III) ion is eight coordinate. It is bonded with four bidentate  $N,N,N',N'$ -tetraethylmalonamide units from two different molecules of the ligand (Fig. 30).



**Figure 30** – The structure of  $[\text{NdL}_2] \cdot (\text{ClO}_4)_3 \cdot \text{C}_2\text{H}_5\text{OH}$  (**18**):

**a** – ORTEP drawing (30% probability ellipsoids); carbon – gray, oxygen – red, nitrogen – blue, hydrogen – white, chlorine – green; molecules of solvent ( $\text{C}_2\text{H}_5\text{OH}$ ) have been omitted for clarity; **b** – chemical diagram of the cation  $[\text{NdL}_2]^{3+}$  of **18**.

The coordination polyhedron of Nd is a distorted square antiprism (Fig. 31).



**Figure 31** – The coordination polyhedron of the  $\text{Nd}^{3+}$  ion in **18** (square antiprism):

**a** – side view; **b** – top view.

In contrast to nitrate ions in the crystal structures **15**, **16** and **17** the perchlorate ions in **18** are located outside the inner coordination sphere of neodymium(III), i.e. they are non-coordinating. The metal-to-ligand stoichiometric ratio in **18** equals 1:2.

The closest structural analogues of **18** reported in the literature are the hexafluorophosphate salts of the tetrakis(*N,N,N',N'*-tetramethylmalonamide) complexes of samarium(III) and erbium(III) [133] and the perrhenate salt of the tetrakis(*N,N,N',N'*-tetraethylmalonamide) complex of neodymium(III) [134]. In these complexes the metal ions have coordination environments, which are formed by carbonyl oxygen atoms of four bidentate malonamide ligands, with the same geometry (i.e. square antiprisms) as that found in **18**.

The reduction of the Nd(III) coordination number when changing from the structure **15** to **18** is accompanied by a decrease in the bond distances of neodymium(III) with the carbonyl oxygen atoms of

the *N,N,N',N'*-tetraethylmalonamide units from [2.415(3) – 2.530(4)] Å in **15** to [2.384(3) – 2.478(4)] Å in **18**. However these distances are the shortest in the structure **16**: [2.357(2) – 2.421(2)] Å and [2.361(3) – 2.417(3)] Å.

Although perchlorate based industrial solvent extraction systems for metals may not be attractive for safety reasons, this weakly-coordinating anion can be used to provide valuable structural information from its complexes with metals. Thus the structure **18** proves that the bismalonamide ligand **8** can be tetradentate in the complexes with the lanthanides.

*On the denticity of the bismalonamide 8 in its crystal complexes with lanthanides(III).*

Each of the crystal structures **15** – **18** has a specific coordination of the *ortho*-bismalonamide **8** with a lanthanide(III) ion. This illustrates the complexity and diversity of the coordination chemistry of the bismalonamide ligands. The analyzed structures provoked the question of the denticity of the *ortho*-bismalonamides in their complexes with trivalent lanthanides. In the structure Ce(NO<sub>3</sub>)<sub>3</sub>·L<sub>2</sub> (**17**) bismalonamide **8** acts as a bidentate ligand, being an equivalent of a conventional bidentate malonamide in the sense of the metal coordination. Thus, despite possessing four potentially coordinating carbonyl oxygen atoms, bismalonamide **8** coordinates with cerium(III) atoms by only two oxygen atoms in the structure **17**. Therefore no entropy-induced free Gibbs energy gain can be expected for such coordination. In the crystal complex [NdL<sub>2</sub>]·(ClO<sub>4</sub>)<sub>3</sub>·C<sub>2</sub>H<sub>5</sub>OH (**18**) bismalonamide **8** is tetradentate. Both malonamide units of the ligand are involved in coordination with neodymium(III) central ion. This structure presents the first reported crystallographic evidence of the tetradentate coordination of the bismalonamides with trivalent lanthanides. The coordination of **8** with Nd(III) ions in the structures [Nd<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>·L<sub>2</sub>]·(CH<sub>3</sub>CN)<sub>3</sub> (**15**) and [Nd<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>L<sub>2</sub>]·[Nd(NO<sub>3</sub>)<sub>5</sub>]·(CH<sub>3</sub>CN)<sub>1.5</sub> (**16**) is intermediate between the coordination modes in **17** and **18**. In the structures **15** and **16** each neodymium(III) ion is bonded to two bidentate malonamide groups from two molecules of **8**, like central cerium(III) ion in **17**. Hence bismalonamide **8** is the bidentate ligand in the structures **15** and **16** with respect to an individual Nd(III) ion. However the structures **15** and **16** are composed of the macrocyclic dimers. Both malonamide groups of each molecule of **8** are involved in the coordination with Nd(III) ions in these dimers, which means that bismalonamide **8** is tetradentate in **15** and **16**, though not coordinating to one central ion with all four carbonyl oxygen atoms.

An important conclusion can be drawn from the structures **15** – **18** regarding the effect of a counter-ion on the coordination of the *ortho*-bismalonamides with trivalent lanthanides. In the structure **18** perchlorate anions do not coordinate with a lanthanide(III) ion, thus allowing bismalonamide ligands to occupy its coordination sites. Bidentate ( $\kappa^2O$ -NO<sub>3</sub>) and tridentate ( $\mu$ - $\kappa^1O$ - $\kappa^2O$ ,  $O'$ -NO<sub>3</sub>) nitrate anions in the structures **15**, **16** and **17** do coordinate to a lanthanide(III) ion and occupy five to six coordination sites of it, reducing (but not eliminating) the chances of the *ortho*-bismalonamide **8** for a polydentate coordination with a metal ion. In general the polydentate coordination mode of the bismalonamides with trivalent lanthanides should be more common for a medium with a weakly coordinating counter-ion.

Single-crystal XRD analysis of the structures **15** – **18** provides the information on their compositions. The stoichiometric ratio between neodymium(III) and bismalonamide **8** in the structure **15** and in the cation of **16** is 2:2, however it is reduced to 1:1 if the empirical metal-to-ligand ratio is considered. The structures **17** and **18** have the identical 1:2 lanthanide(III)-bismalonamide **8** stoichiometric ratios in spite of the fact that the coordination modes in these complexes are different. The slope analysis, routinely used to establish the composition of the extracted metal species [7], would be incapable of neither the recognition of the dimeric character of the lanthanide species in **15** and **16** nor the distinguishing between the structures in the pairs **15** – **16** and **17** – **18** with the isostoichiometric compositions.

### 6.3.3 Stoichiometry of the lanthanide(III) complexes with tetraamide **8** in solutions

The analysis of the structures **15** – **18** with single-crystal XRD revealed the coordination of trivalent lanthanide ions with tetraamide **8** in a solid state. To be able to know how far the collected crystallography data can be applied for an explanation of a solvent extraction of lanthanides with the *ortho*-bismalonamides such as tetraamide **5**, the speciation of the solution-state metal complexes with a bismalonamide ligand is needed.

In the method of slow solvent evaporation, used to obtain crystal structures **15** – **18**, a solid-state metal complex (i.e. a crystal) is evolving under continuous exchange of a matter with solution-state metal complexes. Therefore the speciation in the solution-state complexes is best established from an examination of a mother liquor for the respective crystals.

In this work the speciation analysis of the lanthanide(III)-bismalonamide complexes was carried out by electrospray ionization – mass spectrometry (ESI-MS) for those acetonitrile solutions that were used to prepare the single-crystals. The solutions were diluted with acetonitrile before the measurements as required by the method.

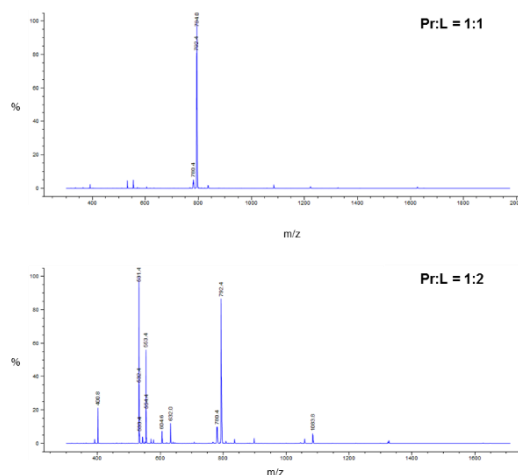
The ESI-MS technique can be used to investigate the metal-ligand interactions, namely to determine precisely the composition of the complexes in solutions, because it enables to preserve and transport metal-ligand complexes from a solution to a gas phase [75, 135, 136].

Since neodymium is a central atom in the crystal structures **15** and **16**, this metal was selected for the ESI-MS analysis of its nitrate complexes with bismalonamide **8** in acetonitrile solutions. However the complicated isotopic composition of neodymium, which has seven naturally occurring isotopes: Nd-142 (27.13 %), Nd-143 (12.18 %), Nd-144 (23.80 %), Nd-145 (8.30 %), Nd-146 (17.19 %), Nd-148 (5.76 %), Nd-150 (5.64 %) [137], makes the recorded ESI-mass spectra of its complexes with **8** being inconvenient for analysis (Fig. A1 and A2). On the other hand praseodymium, adjacent to neodymium in the Periodic Table of the Elements, has very similar chemical properties and therefore should form solution-state complexes of the same composition. Naturally occurring praseodymium has only one isotope Pr-141 (100 %) [137], which facilitates the analysis of the ESI-mass spectra. The ESI-mass spectra of the praseodymium(III) complexes with bismalonamide **8** were recorded in acetonitrile and compared with those for neodymium. This comparison demonstrated that the speciation of the lanthanide(III) complexes is identical for both metal ions. For the sake of conciseness only the ESI-mass spectra of praseodymium(III) complexes with bismalonamide **8** are discussed further.

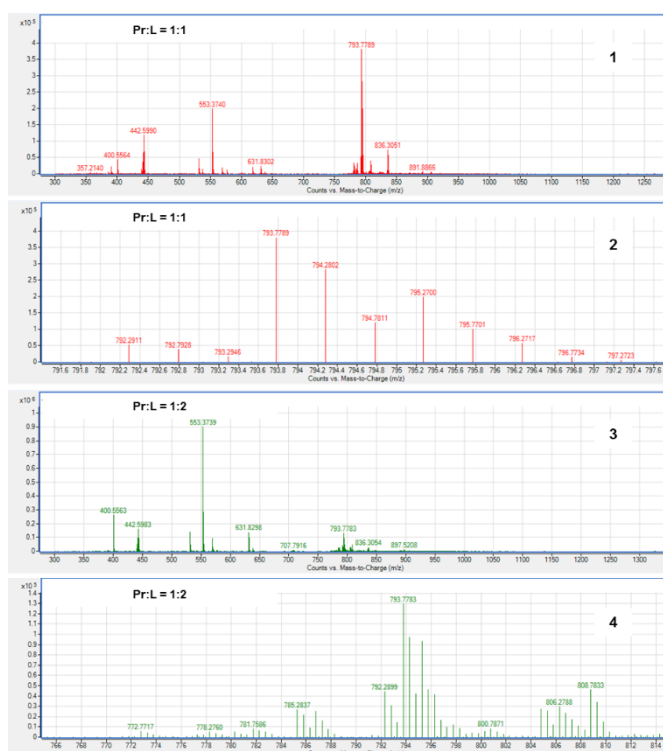
Positive electrospray ionization – mass spectra (Fig. 32) were recorded for the bismalonamide **8** solution and for two solutions of Pr(III) nitrate and bismalonamide **8** with the (1:1) and (1:2) metal-to-ligand molar ratios, respectively. Three groups of peaks were detected in the mass spectrum of bismalonamide **8** (L) in acetonitrile (Fig. A3). The peaks at  $m/z = 531.4$  and  $532.4$  correspond to the protonated form of the ligand  $[LH]^+$ . The peaks at  $m/z = 553.4$  and  $554.4$  are assigned to the sodium complex with the ligand  $[LNa]^+$ . The less abundant species having  $m/z = 604.6$  and  $605.6$  were not identified. All these peaks can be observed in both solutions of praseodymium(III) having the (1:1) and (1:2) metal-to-ligand molar ratios (Fig. 32). When the initial concentration of the ligand is high enough, like in the solution with Pr:L = 1:2, one more sodium complex with the ligand  $[L_2Na]^+$  ( $m/z = 1083.8$ ) is being formed. It is worth mentioning here that the  $H^+$  ions come from acetic acid added to the samples, while  $Na^+$  is leached out from glass.

In the equimolar (1:1) solution of praseodymium and the ligand the complexes with  $m/z = 792.4$  and  $794.0$  are dominating (Fig. 32). However the formation of the minor species with  $m/z = 780.4$  was also noticed. The spectrum of the solution with the higher fraction of the ligand, i.e. with Pr:L = 1:2, is more diverse and contains peaks of the complexes with  $m/z = 400.8$ ;  $632.0$ ;  $780.4$  and  $792.4$  (Fig. 32). In order

to identify these species positive high-resolution ESI-mass spectra of the praseodymium(III) complexes were recorded for both solutions (Fig. 33).



**Figure 32** – Positive ESI-mass spectra of the solutions of  $\text{Pr}(\text{NO}_3)_3$  and bismalonamide **8** (**L**) with the (1:1) and (1:2) metal-to-ligand molar ratios.



**Figure 33** – Positive high-resolution ESI-mass spectra of the solutions of  $\text{Pr}(\text{NO}_3)_3$  and bismalonamide **8** (**L**) with the (1:1) (image **1**) and (1:2) (image **3**) metal-to-ligand molar ratios. The images **2** and **4** are the expansions of the spectra **1** and **3**, respectively.

The identified praseodymium(III) species are listed in Table 12.

All  $\text{Pr}(\text{III})$  complexes with bismalonamide **8**, detected by ESI-MS, have the metal-to-ligand molar ratios of either (1:1) or (1:2), with one exception of the (1:3) ratio in  $[\text{PrL}_3\text{NO}_3]^{2+}$ . This complex with unusual stoichiometry was observed only in the  $\text{Pr}(\text{III})$  solution with higher initial concentration of the ligand.

**Table 12** – Praseodymium(III) complexes with bismalonamide **8** (L) detected by electrospray ionization – mass spectrometry (ESI-MS) in acetonitrile.

Complex	Exact mass, a.m.u.	$m/z$		$\Delta(m/z)^*$ , ppm	Mass intensity (theor.), %
		experimental	theoretical		
$[\text{PrL}_3\text{NO}_3]^{2+}$	1794.0451	897.5208	897.0226	-	100.0
			897.5243	3.9	97.3
$[\text{PrL}_2]^{3+}$	1201.6741	400.5564	400.5580	4.0	100.0
			400.8925	-	64.9
			401.2269	-	20.7
$[\text{PrL}_2\text{NO}_3]^{2+}$	1263.6619	631.8302	631.8310	1.3	100.0
			632.3327	-	64.9
			632.8343	-	20.7
$[\text{PrL}_2(\text{NO}_3)_2]^+$	1325.6497	1320-1330	1325.6498	-	100.0
			1326.6531	-	64.9
			1327.6565	-	20.7
$[\text{PrL}(\text{NO}_3)_2]^+ **$	795.2665	795.2700	795.2666	4.3	100.0
		796.2717	796.2699	2.3	32.4
		797.2733	797.2733	0.0	5.1
$[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$	1590.5330	795.2700	795.2666	4.3	100.0
		795.7701	795.7682	2.4	64.9
		796.2717	796.2699	2.3	20.7
		796.7734	796.7659	9.4	4.3
$[\text{Pr}_2\text{L}_2(\text{NO}_3)_3(\text{CH}_3\text{COO})]^{2+}$	1587.5585	793.7789	793.7793	0.5	100.0
		794.2802	794.2810	1.0	67.1
		794.7811	794.7826	1.9	22.1
$[\text{PrL}(\text{NO}_3)(\text{CH}_3\text{COO})]^+ **$	792.2920	792.2899	792.2920	2.7	100.0
		793.2921	793.2954	4.2	34.6
$[\text{Pr}_2\text{L}_2(\text{NO}_3)_2(\text{CH}_3\text{COO})_2]^{2+}$	1584.5840	792.2911	792.2920	1.1	100.0
		792.7928	792.7937	1.1	69.2
		793.2946	793.2954	1.0	23.6

$$* \Delta(m/z) = \left| \frac{(m/z)_{\text{theor.}} - (m/z)_{\text{exper.}}}{(m/z)_{\text{theor.}}} \right| \times 10^6$$

\*\* - possible species

As one can expect the dominating species in the equimolar (1:1) solution of praseodymium and bismalonamide **8** have the equimolar (1:1) metal-to-ligand empirical ratio. However these complexes surprisingly were found to be the dimers  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$ ,  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_3(\text{CH}_3\text{COO})]^{2+}$  and  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_2(\text{CH}_3\text{COO})_2]^{2+}$  with the (2:2) metal-to-ligand stoichiometry (Table 12). The complex  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_3(\text{CH}_3\text{COO})]^{2+}$  has the highest relative concentration among other dimers in the solution. The collected high-resolution ESI-MS spectra of the dimeric species allow one to distinguish them clearly from all other detected or hypothetical praseodymium(III) complexes with the ligand e.g. mononuclear species or polymers of the higher order (trimers, tetramers *etc.*). The minor species  $[\text{PrL}_2]^{3+}$  and  $[\text{PrL}_2(\text{NO}_3)_2]^+$  were also detected in the solution (Fig. 33).

In the acetonitrile solution with the (1:2) initial molar ratio of praseodymium(III) to bismalonamide **8** the dimers  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$ ,  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_3(\text{CH}_3\text{COO})]^{2+}$  and  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_2(\text{CH}_3\text{COO})_2]^{2+}$  remain to be one of the major metal species (Fig. 32). However the fractions of the (1:2) ligand-rich complexes  $[\text{PrL}_2]^{3+}$  and  $[\text{PrL}_2\text{NO}_3]^{2+}$  are higher in this solution than in the equimolar solution with  $\text{Pr}:\text{L} = 1:1$  (Fig. 33). It can be explained by the right shift of the praseodymium(III)-bismalonamide **8** reaction equilibria (20) and (21) in the  $\text{Pr}:\text{L} = 1:2$  solution, caused by an increase of the initial ligand concentration at fixed initial concentration of the metal:



The presence of the praseodymium(III) dimeric complexes in both solutions obscures the formation of the corresponding mononuclear species  $[\text{PrL}(\text{NO}_3)_2]^+$  and  $[\text{PrL}(\text{NO}_3)(\text{CH}_3\text{COO})]^+$ . Thus the ESI-MS spectrum of the monomer  $[\text{PrL}(\text{NO}_3)_2]^+$  fully coincides with that of the dimer  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$  for the exception of two peaks at  $m/z = 795.7701$  (theoretical mass intensity 64.9 %) and 796.7734, which are both attributed exclusively to the dimer. Therefore it is hard to confirm or rule out the existence of the mononuclear species  $[\text{PrL}(\text{NO}_3)_2]^+$  in the acetonitrile solutions. However from the experimental ratios of intensities of the  $m/z$  peaks of the dimers it is clear that the mononuclear complexes, if they do exist in the solutions, could be minor species only. This conclusion is applicable to the complex  $[\text{PrL}(\text{NO}_3)(\text{CH}_3\text{COO})]^+$  for the same reasons.

### 6.3.4 Comparison of the single-crystal XRD and ESI-MS results

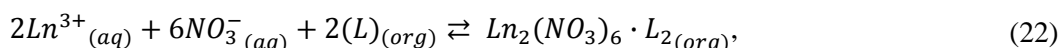
Murillo *et al.* has demonstrated earlier that the bismalonamide ligands can extract europium(III) ions from aqueous solutions with higher distribution ratios than the related bidentate malonamides [11]. It was suggested by Murillo *et al.* that higher distribution ratios of lanthanides(III) in the extraction reactions with the bismalonamides could result from favorable entropy changes in these reactions, assuming that the bismalonamides were extracting trivalent lanthanide ions as the tetradentate ligands [11]. However neither of these two hypotheses have been tested experimentally. So far no research has been conducted on the coordination of the ligands with multiple malonamide functional groups, including bismalonamides, with lanthanide(III) ions, which is regarded as the obstacle for the development of this type of solvent extraction ligands [11].

In this work single-crystal XRD and ESI-MS analyses of the lanthanide(III) complexes with the *ortho*-bismalonamide **8** were conducted to compare the complexation of **8** in the solid and solution states. It was intended to use this data to explain the extraction of lanthanides(III) with the *ortho*-bismalonamide **5**. Firstly it is important to decide if the collected crystallographic results are relevant to solvent extraction of lanthanides. To determine if the formation of the solid species was due to crystal packing effects the ESI-mass spectroscopy experiments were performed using solutions identical to those used

for growing the crystals. It is assumed that the dimers  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$ ,  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_3(\text{CH}_3\text{COO})]^{2+}$  and  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_2(\text{CH}_3\text{COO})_2]^{2+}$ , existing in acetonitrile solutions, are related to the dimers in the crystal structures  $[\text{Nd}_2(\text{NO}_3)_6 \cdot \text{L}_2] \cdot (\text{CH}_3\text{CN})_3$  (**15**) or  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2] \cdot [\text{Nd}(\text{NO}_3)_5] \cdot (\text{CH}_3\text{CN})_{1.5}$  (**16**). The complexes  $[\text{PrL}_2]^{3+}$ ,  $[\text{PrL}_2\text{NO}_3]^{2+}$  and  $[\text{PrL}_2(\text{NO}_3)_2]^+$ , detected by the ESI-MS in acetonitrile, are likely related to the crystal structures  $\text{Ce}(\text{NO}_3)_3 \cdot \text{L}_2$  (**17**) or  $[\text{Nd} \cdot \text{L}_2] \cdot (\text{ClO}_4)_3 \cdot \text{C}_2\text{H}_5\text{OH}$  (**18**). The observation of the species by both single-crystal XRD and ESI-MS techniques allows one to conclude that the crystal structures **15** – **18** are not formed due to a specific feature of the crystallization process.

It is important to mention that the lanthanide(III) complexes, identified by single-crystal XRD and ESI-MS, are formed under specific experimental conditions i.e. high metal-to-ligand ratios, which are not typical for solvent extraction of the metal ions. Therefore caution must be taken when the XRD and ESI-MS data is applied for an explanation of a solvent extraction of metal ions. It might be possible to observe the existence of polynuclear species, including dimers, by performing the solvent extraction tests. The formation of the solution-state polynuclear complexes and aggregates of lanthanides with conventional bidentate malonamide ligands at high metal concentrations has been described by Ellis *et al.* [72, 73] and Antonio *et al.* [138].

The formation of the dimers, such as  $[\text{Pr}_2\text{L}_2(\text{NO}_3)_4]^{2+}$ , in an organic phase of an extraction system can be described by the reaction equation for a nitrate medium:



where Ln and L represent a lanthanide ion and a bismalonamide molecule, respectively, and the subscripts (aq) and (org) correspond to the aqueous and the organic phases of the extraction system, respectively. The apparent equilibrium constant  $K_{ex}$  of the reaction (22) is defined by the equation:

$$K_{ex} = \frac{[\text{Ln}_2(\text{NO}_3)_6 \cdot \text{L}_2]_{org}}{[\text{Ln}^{3+}]_{aq}^2 \times [\text{NO}_3^{-}]_{aq}^6 \times [\text{L}]_{org}^2}, \quad (23)$$

where the square brackets stand for the analytical concentrations of the corresponding species at equilibrium. The distribution ratio (D) of a lanthanide ion is described by the equation:

$$D = \frac{2 \times [\text{Ln}_2(\text{NO}_3)_6 \cdot \text{L}_2]_{org}}{[\text{Ln}^{3+}]_{aq} \times (1 + \beta_1 \times [\text{NO}_3^{-}]_{aq} + \beta_2 \times [\text{NO}_3^{-}]_{aq}^2)}, \quad (24)$$

where  $\beta_1$  and  $\beta_2$  are the stability constants of the nitrate complexes of Ln(III) in an aqueous phase.

From the equations (23) and (24) one can derive a new equation, which suggests that a distribution ratio of Ln(III) should be proportional to an equilibrium metal concentration in an aqueous phase provided that the dimers are the dominant species in an organic phase:

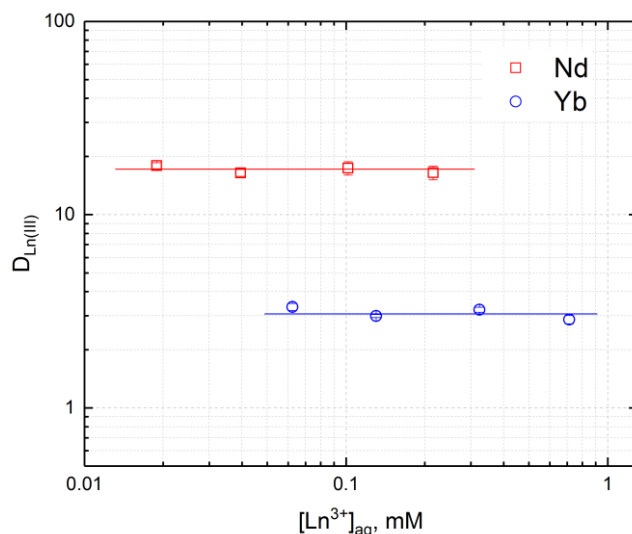
$$D = \left( \frac{2 \times K_{ex} \times [\text{NO}_3^{-}]_{aq}^6 \times [\text{L}]_{org}^2}{1 + \beta_1 \times [\text{NO}_3^{-}]_{aq} + \beta_2 \times [\text{NO}_3^{-}]_{aq}^2} \right) \times [\text{Ln}^{3+}]_{aq}. \quad (25)$$

As long as the nitrate concentration in the aqueous phase remains constant, the complexation of nitrates to a lanthanide ion will not prevent the distribution ratio being proportional to the lanthanide concentration.

The solvent extraction experiment, in which the lanthanide concentration was varied, demonstrated that the distribution ratios of neodymium and ytterbium were not dependent on the equilibrium metal concentration in an aqueous phase (Fig. 34). These results indicate that the dimers of the bismalonamide **5** and lanthanide(III) ions were not being formed under the selected experimental conditions. Also when



the diluent of an organic phase was nitrobenzene no evidence for the Eu(III) dimer formation was observed by solvent extraction (section 6.2).



**Figure 34** – The distribution ratios of Nd(III) and Yb(III) as functions of an equilibrium metal concentration in an aqueous phase. Org. phase: 0.36 M bismalonamide **5** in Solvesso 150 ND. Aq. phase: 3 M HNO<sub>3</sub>. The solid lines are the linear regressions with the slopes = 0. The uncertainty bars are at  $\pm 1\sigma$ .

It can be reasoned that the formation of the dimers in acetonitrile is governed by concentrations of a metal and the ligand **8** (Fig. 32 and 33). In solvent extraction processes the dimers might be formed only at high metal loading of an organic phase.

#### 6.4 Effects of structure of the bismalonamides on extraction of lanthanides(III)

It was discussed in section 4 that the amide extractants with multiple malonamide ligating groups are assembled from either two (bismalonamides) or three (trismalonamides) molecules of conventional bidentate malonamides by bonding them by a linker, called a platform, into one molecule. It was demonstrated by Murillo *et al.* and Dam *et al.* that in the reactions of lanthanide(III) and actinide(III) extraction distribution ratios of the metal ions depend on the constitution of these ligands, namely on the structures of a platform (e.g. Table 4) and a malonamide ligating group [11, 38]. The effects of structure of a xylylene platform and *N*-alkyl substituents of the bismalonamide extractants (Table 13) on distribution ratios of lanthanides(III) were investigated.

##### 6.4.1 The effect of a xylylene platform structure in the bismalonamides on extraction of lanthanides(III)

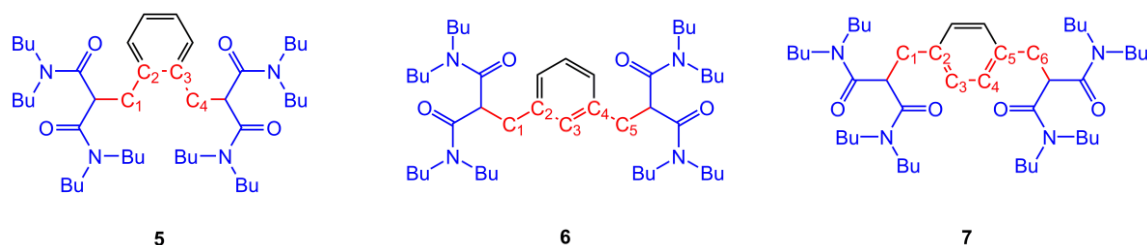
It was suggested (section 6.2) that in the extracted complexes bismalonamide **5** is bound to a lanthanide(III) ion in a tetradentate coordination mode. This type of coordination was observed in the crystal structure **18** for a Nd(III) ion and bismalonamide **8**, which is the homologue of **5**. The bismalonamides **5** and **8** both have the *ortho*-xylylene platform (Table 13). A platform of a bismalonamide controls the distance between two malonamide ligating groups. Therefore it may influence the coordination of a bismalonamide with lanthanides and consequently the distribution ratios of these metals in the extraction reactions.

Three bismalonamides **5**, **6** and **7** were prepared (Table 13). They are the structural isomers, having the isomeric *ortho*-, *meta*- and *para*-xylylene platforms, respectively.

**Table 13** – The constitution characteristics of the *C*-alkylated bismalonamides **5** – **8** and the bidentate malonamide **2**.

Designation number	Molecular structure	Platform	Ligating group ( <i>N</i> -alkyl substituents)	Number of ligating groups
8		 <i>ortho</i> -xylylene	 (C <sub>2</sub> H <sub>5</sub> )	2
5			 ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )	
6				
7		<i>para</i> -xylylene		
2		 benzyl		1

Two *N,N,N',N'*-tetrabutylmalonamide groups in the molecules of **5**, **6** and **7** are separated from each other by four, five and six carbon atoms of a platform, respectively (Fig. 35).



**Figure 35** – Molecular structures of the isomeric bismalonamides **5** – **7**.

*N,N,N',N'*-tetrabutylmalonamide ligating groups are shown in blue.

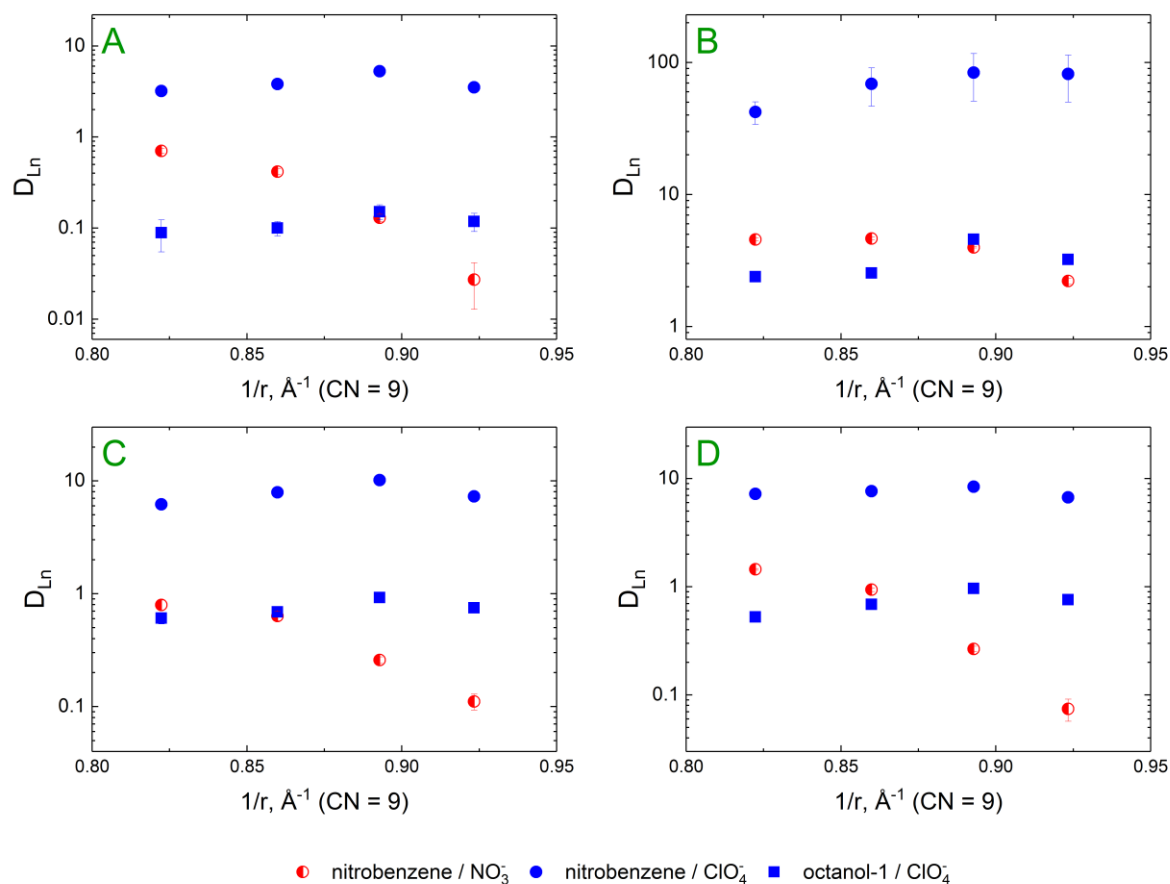
The fragments of a xylylene platform, separating two ligating groups, are shown in red.

The bismalonamides **5**, **6** and **7** were compared with each other and with the reference bidentate malonamide **2** (Table 13) in the reactions of lanthanide(III) extraction in order to investigate the effect

of a platform structure on distribution ratios of the metal ions. The extraction reactions were conducted using either perchlorate or nitrate medium of an aqueous phase.

The bismalonamide **7** was found to be insoluble (or sparingly soluble) in non-polar diluents such as Solvesso 150 ND. All bismalonamides **5** – **7** and the malonamide **2** were soluble in nitrobenzene and in 1-octanol. These were used as the diluents of the organic phases. Both diluents are polar. However nitrobenzene is the aromatic compound while 1-octanol is the aliphatic one.

The diluent of an organic phase affects the distribution ratios of the lanthanides(III) in the reaction with **5** – **7** and **2** (Fig. 36).



**Figure 36** – The distribution ratios of the lanthanides(III) as functions of the reciprocal of their ionic radii. The org. phases: 0.1 M amide in nitrobenzene (blue and red circles) or 1-octanol (squares); the amide: **A** – **2**, **B** – **5**, **C** – **6**, **D** – **7**. The aq. phases: 1.4 mM La, 1.4 mM Nd, 1.3 mM Eu, 1.2 mM Dy; 0.1 M  $\text{HNO}_3$  and 3 M  $\text{NH}_4\text{NO}_3$  (red circles) or 0.1 M  $\text{HClO}_4$  and 3 M  $\text{NaClO}_4$  (blue circles and squares). The uncertainty bars are at  $\pm 1\sigma$ .

In the extraction reactions with each of the four amides (**5**, **6**, **7**, **2**) and the perchlorate medium in the aqueous phases, the distribution ratios of the lanthanides decreased when the diluent of the organic phases has been changed from polar nitrobenzene to less polar 1-octanol (Fig. 36). No extraction of the lanthanides was observed in the reactions with each of the four amides when using the nitrate medium in the aqueous phases and 1-octanol as the diluent of the organic phases. The effect of the polarity of a diluent of an organic phase on distribution ratios of the metal ions can be associated with more substantial contribution of the charge-separated resonance forms (Fig. 1) of the amides **5**, **6**, **7**, and **2** in the media with higher dielectric constants [41, 77]. The formation of the polar extracted species, i.e. the

solvent-separated ion pairs [7, 139], could be the alternative explanation of this diluent effect at least for the reactions with the perchlorate medium of the aqueous phases.

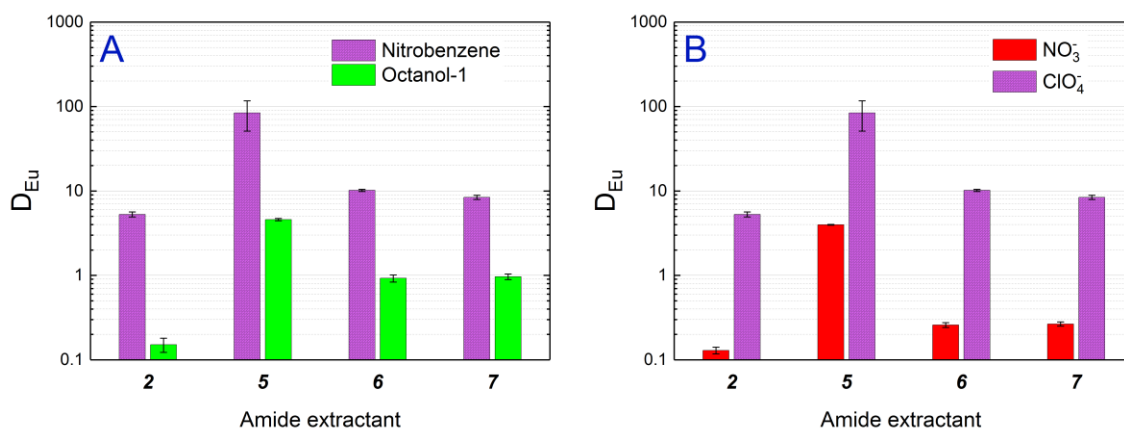
The medium of the aqueous phases also has the influence on the distribution ratios of the lanthanides (Fig. 36). In the extraction reactions with each of the four amides (**5**, **6**, **7**, **2**) and nitrobenzene as the diluent of the organic phases the distribution ratios of the lanthanides increased when the nitrate medium of the aqueous phases has been changed to the perchlorate one (Fig. 36). Both nitrate and perchlorate anions are singly charged. The calculated ionic radii in aqueous solutions are 0.177 nm for  $\text{NO}_3^-$  and 0.241 nm for  $\text{ClO}_4^-$  [140]. Hence the perchlorate anion has lower charge density, i.e. the ratio of the electrostatic charge of the ion and its ionic radius, and, accordingly, higher lipophilicity than the nitrate anion. This fact can be illustrated by the standard Gibbs energies of the ion partitioning between water and nitrobenzene, which are equal to 24.2 kJ/mol for  $\text{NO}_3^-$  and 7.4 kJ/mol for  $\text{ClO}_4^-$  [141]. The difference in the lipophilicity of the nitrate and perchlorate anions could explain the medium effect observed in the reactions of the lanthanide(III) extraction.

The relationship between lanthanide distribution ratios and their ionic radii depends on the medium of the aqueous phases (Fig. 36). In the extraction reactions with each of the four amides (**5**, **6**, **7**, **2**), when using the perchlorate medium in the aqueous phases and nitrobenzene as the diluent of the organic phases, the distribution ratios of the lanthanides moderately increase with a decrease of the ionic radii i.e. in the order:  $\text{La} < \text{Nd} < \text{Eu}$  and then slightly decreased for Dy (Fig. 36). This is due to the increase of the charge densities of the lanthanides across the lanthanide series, which causes the stronger bonding of the smaller lanthanide ions with the amides [88] and, consequently, the formation of more stable extracted complexes. The perchlorate anions are likely not coordinating with lanthanides as one can see in e.g. the crystal structure **18**. The deviation of the distribution ratios of dysprosium, which is the smallest lanthanide among the four studied ions, from the order of the extraction selectivity could be explained by the steric crowding of the first order [91], i.e. by the ligand crowding in the inner coordination sphere of a Dy ion. The steric crowding could weaken the extracted complexes of Dy.

In contrast in the extraction reactions with each of the four amides (**5**, **6**, **7**, **2**), when using the nitrate medium in the aqueous phases and nitrobenzene as the diluent of the organic phases, the distribution ratios of the lanthanides decreased with the decrease of the ionic radii i.e. in the order:  $\text{La} > \text{Nd} > \text{Eu} > \text{Dy}$  (Fig. 36). This order of the extraction selectivity can result from the effect of the steric crowding of the first coordination sphere of the lanthanide ions. In contrast to the perchlorate anions the nitrate anions do contribute to the steric crowding effect along with the amide ligands, since as a rule they are bound directly to lanthanides(III) in the extracted species, as one can see e.g. in the crystal structures **15** – **17**. It can be concluded that in the studied extraction reactions with the nitrate medium in the aqueous phases the steric crowding effect governs the selectivity of the lanthanide(III) extraction with respect to their ionic radii.

These results are consistent with the data obtained by Musikas *et al.*, who studied the reactions of Am(III) and Eu(III) extraction with *N,N'*-dimethyl-*N,N'*-dioctylmalonamide from nitrate and perchlorate media into *tert*-butylbenzene [56].

It has been demonstrated that the amides **5**, **6**, **7** and **2** display similar trends in the studied extraction reactions (Fig. 36), which is due to the fact that these malonamide extractants have the identical *N,N,N',N'*-tetrabutylmalonamide ligating groups (Table 13). However the amides **5**, **6**, **7** and **2** have different platforms, carrying either one or two ligating groups (Table 13). The structure of a platform affects the distribution ratios of the lanthanides(III) in the reactions with these amides (Fig. 37).



**Figure 37** – The distribution ratios of Eu(III) in the extraction reactions with the amides **2**, **5**, **6**, **7**. (A) The org. phases: 0.1 M amide in nitrobenzene or 1-octanol. The aq. phase: 0.1 M  $HClO_4$  and 3 M  $NaClO_4$ . (B) The org. phase: 0.1 M amide in nitrobenzene. The aq. phases: 0.1 M  $HClO_4$  and 3 M  $NaClO_4$  (the perchlorate medium) or 0.1 M  $HNO_3$  and 3 M  $NH_4NO_3$  (the nitrate medium). The aq. phases in (A) and (B) contain: 1.4 mM La, 1.4 mM Nd, 1.3 mM Eu, 1.2 mM Dy. The uncertainty bars are at  $\pm 1\sigma$ .

In all studied extraction reactions the distribution ratios of the lanthanides decreased in the order of the amide extractants: **5** > **6**  $\approx$  **7** > **2** (Fig. 37). The distribution ratios of the lanthanides(III) were higher in the reactions with each of the three isomeric bismalonamides **5**, **6** and **7** than in the reactions with the bidentate malonamide **2**. There was little difference between the distribution ratios of the lanthanides in the reactions with bismalonamides **6** and **7** (Fig. 37), indicating the absence of the platform structure effect in these reactions. It allowed one to assume that bismalonamides **6** and **7** have identical mode of coordination with lanthanides(III) in the extraction reactions. This coordination mode is probably similar to that in the crystal structure **17**.

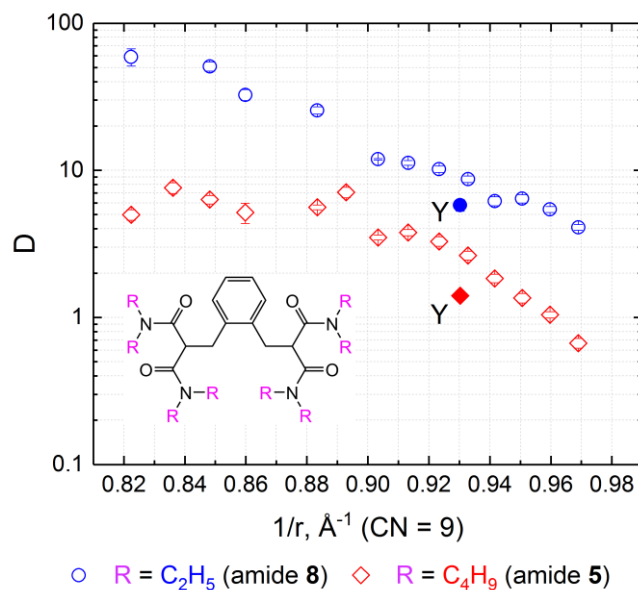
The highest distribution ratios of the lanthanides(III) were obtained in the reactions with bismalonamide **5** (Fig. 37). It is assumed that in these reactions bismalonamide **5** coordinates with lanthanide(III) ions in the tetradentate mode, like its homologue **8** (Table 13) in the crystal structure **18**. This coordination mode is possible due to the shorter distance between two ligating groups in a molecule of **5** compared to the distances in the molecules of its structural isomers **6** and **7** (Fig. 35).

#### 6.4.2 The effect of a length of *N*-(*n*-alkyl) substituents in the *ortho*-bismalonamides on extraction of lanthanides(III) and Y(III)

The structure of substituents at the amide nitrogen atoms of the conventional bidentate malonamides may have strong effect on distribution ratios of trivalent f-block elements (section 4). Two homologous bismalonamides **5** and **8** (Table 13), the molecular structures of which differ from each other only by the length of the *N*-alkyl substituents, being *N*-*n*-butyl ( $n-C_4H_9$ ) in **5** and *N*-ethyl ( $C_2H_5$ ) in **8**, were compared with each other in the reactions of lanthanide(III) and yttrium(III) extraction to investigate the effect of the structure of *N*-alkyl substituents in the bismalonamides on the distribution ratios of the metal ions.

Bismalonamide **8** is insoluble in non-polar diluents, such as Solvesso 150 ND, but it is soluble in nitrobenzene. Therefore the extraction reactions with **5** and **8** were conducted using nitrobenzene as the diluent of the organic phases.

The structure of the *N*-alkyl substituents in the homologous bismalonamides **5** and **8** affects the distribution ratios of the lanthanides(III) and Y(III) in the reactions with these amides (Fig. 38).



**Figure 38** – The distribution ratios of the lanthanides(III) and Y(III) as functions of the reciprocal of their ionic radii. The aq. phase:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; 0.5 M  $\text{HNO}_3$ , 2.5 M  $\text{NH}_4\text{NO}_3$ . The org. phases: 0.1 M amide in nitrobenzene; the amide: **5** (red diamonds) or **8** (blue circles). The closed marks are for Y(III). Distribution ratios of Ce and Eu in the reactions with **8** are omitted due to high values (above 100) with large uncertainties. The uncertainty bars are at  $\pm 1\sigma$ .

In the reactions with bismalonamide **8**, which has shorter *N*-alkyl substituents than bismalonamide **5**, the distribution ratios of the lanthanides(III) and Y(III) were higher (Fig. 38). These results may reflect the steric hindrance effect caused by the *N*-alkyl substituents in the malonamide ligating groups of **5** and **8** upon their complexation with the metal ions. The steric hindrance effect in the extraction reactions of lanthanides(III) with conventional bidentate malonamides was discussed in detail in section 4.

*N*-alkyl substituents in the bidentate malonamides influence two parameters of a reaction of a metal ion extraction: the steric availability of the carbonyl oxygen atoms for a coordination with a metal ion, and the lipophilicity of the extracted metal complexes. The length of the *N*-alkyl substituents in the malonamides has the antagonistic effect on these parameters. Therefore it can be assumed that in the reactions of lanthanide(III) and Y(III) extraction with bismalonamides **5** and **8** the length of the *N*-alkyl substituents has greater impact on the coordination of the extractants with the metal ions than on the lipophilicity of the extracted complexes.

The steric hindrance effect in the extraction reactions is the common phenomenon [7]. It was observed in the extraction reactions of: Eu(III) and Am(III) with *N,N,N',N'*-tetraalkyldiglycolamides [142],  $\text{H}^+$  and U(VI) with *N,N,N',N'*-tetra-*n*-butyl- and *N,N,N',N'*-tetra-*iso*-butylmalonamides [47], U(VI) and Pu(IV) with tri-*n*-butyl- and tri-*iso*-butyl phosphates [7], U(VI) and Pu(IV) with *N,N*-dioctylbutylamide and *N,N*-dioctyl-*iso*-butylamide [7]. The steric hindrance effects in the crystal structures of the lanthanide(III) complexes with the monoamides were discussed by Clement *et al.* [41].

In the extraction reactions with bismalonamides **5** and **8** the distribution ratios of the lanthanides decrease in general with the decrease of the ionic radii (Fig. 38). Such patterns<sup>8</sup> are common for the reactions of lanthanide(III) extraction with the bidentate malonamides from nitrate media [76, 77, 86, 143].

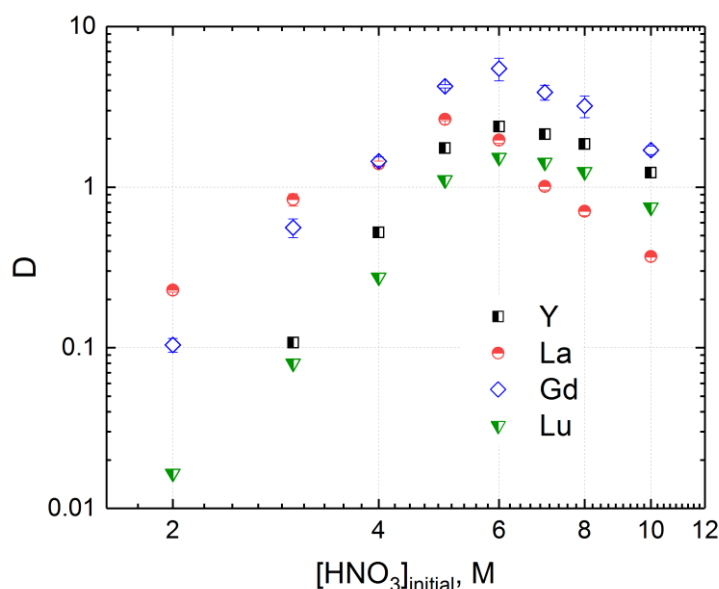
<sup>8</sup> The lanthanide pattern is the dependence of the distribution ratios of the lanthanides(III) on either their atomic numbers or the ionic radii.

## 6.5 Effects of nitric acid concentration on lanthanide(III) extraction with bismalonamide 5

The effect of the nitric acid concentration on the distribution ratios of lanthanides(III) and yttrium(III) in the extraction reactions with bismalonamide **5** was investigated. The pre-equilibration of 0.2 M bismalonamide **5** in Solvesso 150 ND (the organic phase) with (0.2 – 10) M nitric acid solutions (the aqueous phases) demonstrated that a liquid third phase appears if the initial acid concentrations in the aqueous phases exceed 6 moles per liter. The formation of the liquid third phases was suppressed by the addition of 5 % and 10 % (by volume) of 1-decanol to the organic phases, which were contacted with (7 – 8) M and 10 M  $\text{HNO}_3$  solutions, respectively.

There was no extraction of the lanthanides(III) and Y(III) from the aqueous solutions with the nitric acid concentrations below two moles per liter. Neither are extracted the four heaviest lanthanides Er, Tm, Yb and Lu along with Y from the 2 M  $\text{HNO}_3$  solution.

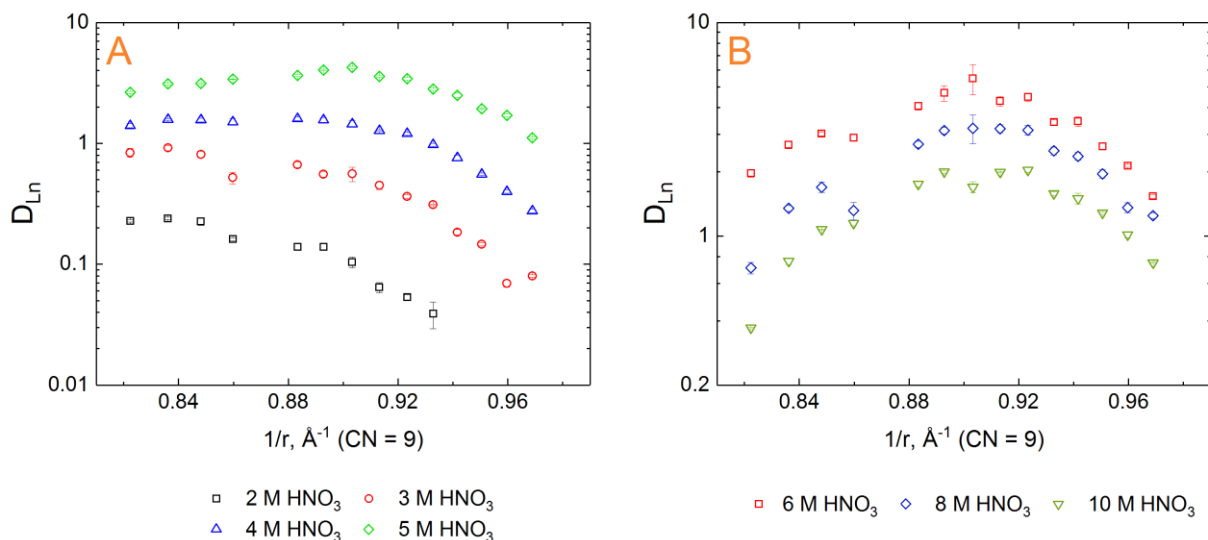
The distribution ratios of the lanthanides(III) and Y(III) increase with the nitric acid concentration increasing from 2 M up to (5 – 6) M  $\text{HNO}_3$  (Fig. 39), which is attributed to the increasing concentration of nitrate anions in the aqueous phases.



**Figure 39** – The dependencies of the distribution ratios of trivalent Y, La, Gd and Lu on an initial nitric acid concentration in the aqueous phases. The aq. phases:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; (2 – 10) M  $\text{HNO}_3$ . The org. phase: 0.18 M tetraamide **5** in Solvesso 150 ND, 10 vol. % 1-decanol. The uncertainty bars are at  $\pm 1\sigma$ .

The distribution ratios decline at higher acid concentrations (Fig. 39). This decline can be explained by the decrease of the free extractant concentration due to nitric acid extraction. The similar dependencies of the distribution ratios on the nitric acid concentration were observed in the lanthanide(III) extraction reactions with conventional bidentate malonamides [19, 56, 59, 77] and are common for neutral extractants [144].

The relationship between lanthanide distribution ratios and their ionic radii depends on nitric acid concentration in the aqueous phases (Fig. 40).



**Figure 40** – The distribution ratios of the lanthanides(III) as functions of the reciprocal of their ionic radii. The aq. phases:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; **A** – (2 – 5) M  $\text{HNO}_3$ ; **B** – (6 – 10) M  $\text{HNO}_3$ . The org. phase: 0.18 M tetraamide **5** in Solvesso 150 ND, 10 vol. % 1-decanol. The uncertainty bars are at  $\pm 1\sigma$ .

The distribution ratios of the lanthanides(III) decrease in general along the lanthanide series from lanthanum to lutetium in the reactions of extraction from the aqueous phases with 2 M and 3 M  $\text{HNO}_3$  (Fig. 40). The similar lanthanide(III) patterns were reported for the reactions of lanthanide(III) extraction with the bidentate malonamides from nitrate media into various diluents [76, 77, 86, 143].

At higher nitric acid concentrations in the aqueous phases, i.e. (4 – 10) M  $\text{HNO}_3$ , the lanthanide patterns acquire a ‘bell’ shape (Fig. 40) with the arbitrary maximum at the midst of the lanthanide series (at Gd or Eu).

The dependencies of the distribution ratios of the lanthanides(III) and Y(III) on the nitric acid concentration in the aqueous phases in the extraction reactions with bismalonamide **5** into Solvesso 150 ND (Fig. 39) suggest that it is possible to perform back-extraction of the metal ions using the aqueous solutions with low nitric acid concentrations. The results of the back-extraction experiment are listed in Table 14.

The effect of the nitric acid concentration on the distribution ratios of lanthanides(III) and yttrium(III) in the extraction reactions with bismalonamide **5** at the constant molar ionic strength in all of the aqueous phases  $I_C = [\text{HNO}_3] + [\text{NH}_4\text{NO}_3] = 6$  M was investigated. In the aqueous phases with the constant ionic strength the concentration of nitrate anions was constant (6 M) while the concentration of the proton ( $\text{H}^+$ ) of nitric acid varied from 0.5 M to 4 M. Ammonium nitrate was used to adjust the concentration of nitrate anions in the aqueous phases to the constant value. The extraction reactions were conducted using either Solvesso 150 ND or nitrobenzene as the diluent of the organic phases.



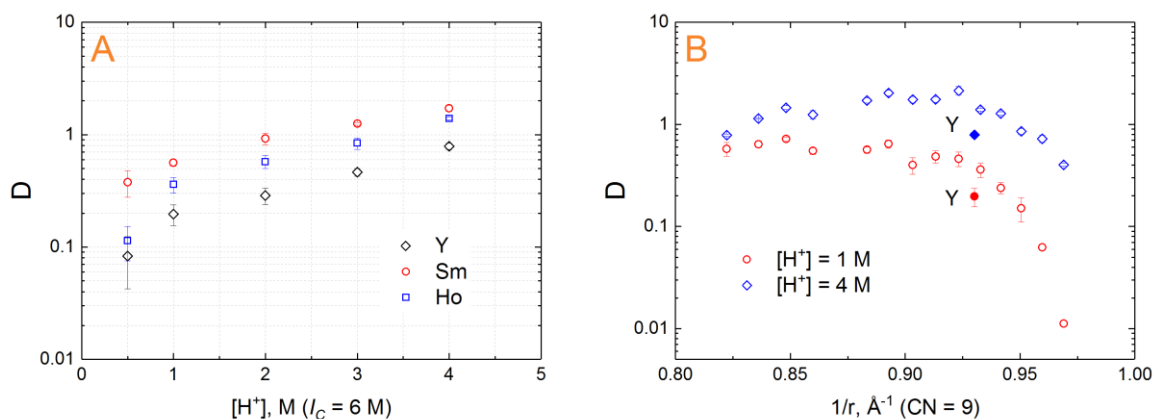
**Table 14** – The percent (E, %) of the back-extracted lanthanides(III) and Y(III). The org. phase: 0.2 M tetraamide **5** in Solvesso 150 ND. The aq. phase for the reaction of extraction:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; 5 M HNO<sub>3</sub>. The aq. phase for the reaction of back-extraction: 0.01 M HNO<sub>3</sub>. In the reaction of back-extraction the phase volume ratio is  $V_{(org)}:V_{(aq)} = 1:2$  and the phase agitation time is 15 min.

Element	Atomic number	E, %	Uncertainties at $\pm 1\sigma$
Y	39	95	1
La	57	99	1
Ce	58	94	3
Pr	59	100	2
Nd	60	100	3
Sm	62	100	2
Eu	63	100	3
Gd	64	83	1
Tb	65	87	2
Dy	66	72	4
Ho	67	100	4
Er	68	74	2
Tm	69	92	2
Yb	70	67	3
Lu	71	88	2

In the reactions with Solvesso 150 ND as the diluent of the organic phases the distribution ratios of the lanthanides(III) and Y(III) increase with the increasing proton (H<sup>+</sup>) concentration of nitric acid in the aqueous phases (Fig. 41). These dependencies indicate that the protons of nitric acid are involved in the reactions of extraction of the metal ions with bismalonamide **5** into Solvesso 150 ND.

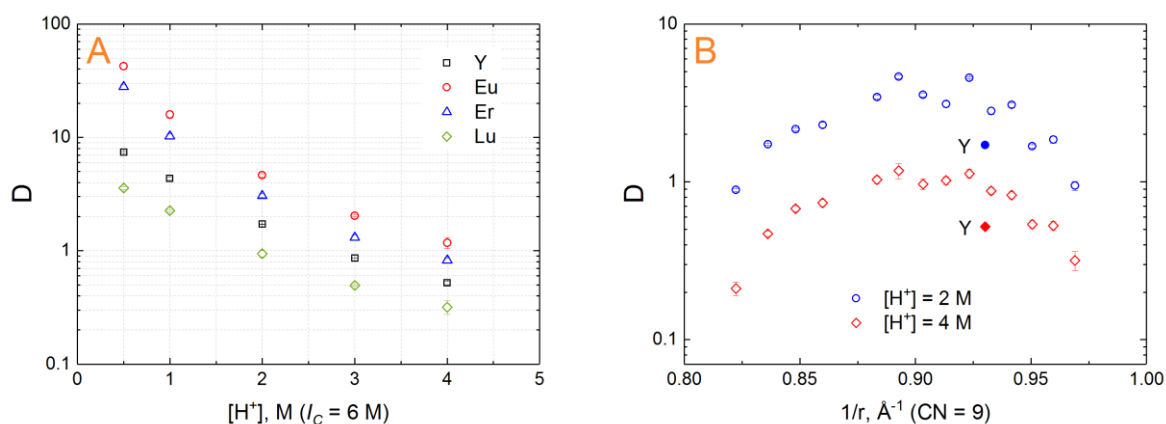
Nigond *et al.* suggested that in the reactions of neodymium(III) and americium(III) extraction with conventional bidentate malonamides from nitrate media into the non-polar hydrocarbons (TPH, benzene), the pregnant organic phases contain a mixture of the acidic  $L_x \cdot M(NO_3)_{(3+y)} \cdot H_{y(org)}$  and non-acidic  $L_2 \cdot M(NO_3)_{3(org)}$  and  $L \cdot M(NO_3)_{3(org)}$  extracted species, where  $M$  is the metal ion (either Nd<sup>3+</sup> or Am<sup>3+</sup>) and  $L$  is a molecule of a malonamide [62, 127, 128].

Chan *et al.* and Spjuth *et al.* postulated that in the extraction reactions of trivalent f-block elements with conventional bidentate malonamides from nitrate media into *tert*-butylbenzene the extracted metal species are predominantly the non-acidic adducts  $L_n \cdot M(NO_3)_{3(org)}$  at the moderate nitric acid concentrations ( $[HNO_3] \leq 1$  M) in the aqueous phases [57-59]. When the nitric acid concentration in the aqueous phases increases further, the dominating extracted species are shifted to the acidic ion pairs  $[H \cdot L]^+ \cdot [M(NO_3)_4]^-_{(org)}$  or  $[H_2 \cdot L]^{2+} \cdot [M(NO_3)_5]^{2-}_{(org)}$ , where  $M$  is the cation of a trivalent f-block element and  $L$  is a molecule of a malonamide [57-59].



**Figure 41** – The dependencies of the distribution ratios of trivalent Y, Sm and Ho on an analytical concentration of the nitric acid proton ( $H^+$ ) in the aqueous phases (A). The distribution ratios of the lanthanides(III) (the opened marks) and Y(III) (the closed marks) as functions of the reciprocal of their ionic radii at  $[H^+] = 1$  M (red circles) or 4 M (blue diamonds) (B). The aq. phases in A and B:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; the constant molar ionic strength  $I_C = [HNO_3] + [NH_4NO_3] = 6$  M. The org. phase: 0.18 M tetraamide **5** in Solvesso 150 ND, 10 vol. % 1-decanol. The uncertainty bars are at  $\pm 1\sigma$ .

In the reactions of extraction of lanthanides(III) and yttrium(III) with bismalonamide **5** from nitrate media into nitrobenzene the distribution ratios of the metal ions decrease with the increasing proton ( $H^+$ ) concentration in the aqueous phases (Fig. 42).



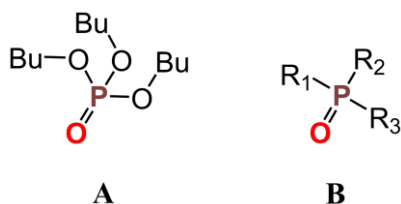
**Figure 42** – The dependencies of the distribution ratios of trivalent Y, Eu, Er and Lu on an analytical concentration of the nitric acid proton ( $H^+$ ) in the aqueous phases (A). The distribution ratios of the lanthanides(III) (the opened marks) and Y(III) (the closed marks) as functions of the reciprocal of their ionic radii at  $[H^+] = 2$  M (blue circles) or 4 M (red diamonds) (B). The aq. phases in A and B:  $(0.100 \pm 0.005)$  mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; the constant molar ionic strength  $I_C = [HNO_3] + [NH_4NO_3] = 6$  M. The org. phase: 0.1 M tetraamide **5** in nitrobenzene. The uncertainty bars are at  $\pm 1\sigma$ .

In this case the protons ( $H^+$ ) of nitric acid inhibit the extraction of the lanthanides(III) and Y(III) most likely due to the competitive coordination with the molecules of bismalonamide **5**. Considering the results of the slope analysis (section 6.3) it is reasonable to assume that the species extracted into nitrobenzene are the non-acidic adducts  $L_2 \cdot M(NO_3)_3(\text{org})$  and  $L \cdot M(NO_3)_3(\text{org})$ , where  $M$  is the lanthanide(III) or Y(III) ion and  $L$  is a molecule of **5**.

It can be concluded that in the reactions of extraction of the lanthanides(III) and yttrium(III) with bismalonamide **5** from nitrate media with the constant ionic strength the effect of the nitric acid concentration on the distribution ratios of the metal ions depends on the diluent of the organic phase. For non-polar Solvesso 150 ND and polar nitrobenzene aromatic diluents this effect is opposite.

## 6.6 Comparison of bismalonamide **5** with the solvating organophosphorus ligands in the extraction reactions of lanthanides(III)

The bismalonamide **5** belongs to the solvating type of extractants, as was confirmed by the single-crystal X-ray diffraction studies (section 6.3). The commercial solvating ligands [7], which are capable of extracting lanthanides(III), are the organophosphorus tri-*n*-butyl phosphate (TBP) and tri-*n*-alkylphosphine oxides (TRPO) (Fig. 43).



**Figure 43** – Molecular structures of the solvating phosphoryl-oxygen extractants: tri-*n*-butyl phosphate (**A**), tri-*n*-alkylphosphine oxide (**B**). The coordinating phosphoryl oxygen atoms are shown in red. Bu stands for *n*-butyl ( $n\text{-C}_4\text{H}_9$ ).  $R_1$ ,  $R_2$  and  $R_3$  designate alkyl groups.

Tri-*n*-butyl phosphate can be used in the large-scale extraction processes for the separation of rare earths from the impurities and into the individual elements in the nitrate media [7, 10]. Tri-*n*-alkylphosphine oxides have been tested for the extraction of actinides, lanthanides(III), and other fission products from nitric acid solutions [145]. These ligands are able to extract trivalent f-block elements from the nitrate media with a moderate acid concentration [115, 145]. The methods for the lanthanide(III) extraction with the commercially available tri-*n*-alkylphosphine oxides, such as CYANEX 923 and CYANEX 921<sup>9</sup>, are under development [146-150].

The bismalonamide **5** was compared with the commercial solvating organophosphorus ligands CYANEX 923 and TBP in the extraction reactions of lanthanides(III).

### 6.6.1 Comparison of bismalonamide **5** with CYANEX 923 in the extraction reactions of lanthanides(III)

The reactions of extraction of the lanthanides(III) with bismalonamide **5** and CYANEX 923 were conducted using either Solvesso 150 ND or methyl isobutyl ketone (MIBK) as the diluents of the organic phases. The organic phases contained 0.37 M bismalonamide **5** or 0.73 M CYANEX 923. These molar concentrations correspond to the 30 % (by volume) concentrations of the extractants in the organic phases<sup>10</sup>. The aqueous phases of the reactions were the 1 M and 3 M solutions of nitric, hydrochloric or sulfuric acid, containing (3.15 – 3.65) mM La, (4.86 – 5.24) mM Ce, (2.95 – 3.40) mM Nd, (0.61 – 0.70) mM Dy and 0.1 mM  $\text{H}_3\text{PO}_4$ . These are the most abundant lanthanides in the geological deposits of the

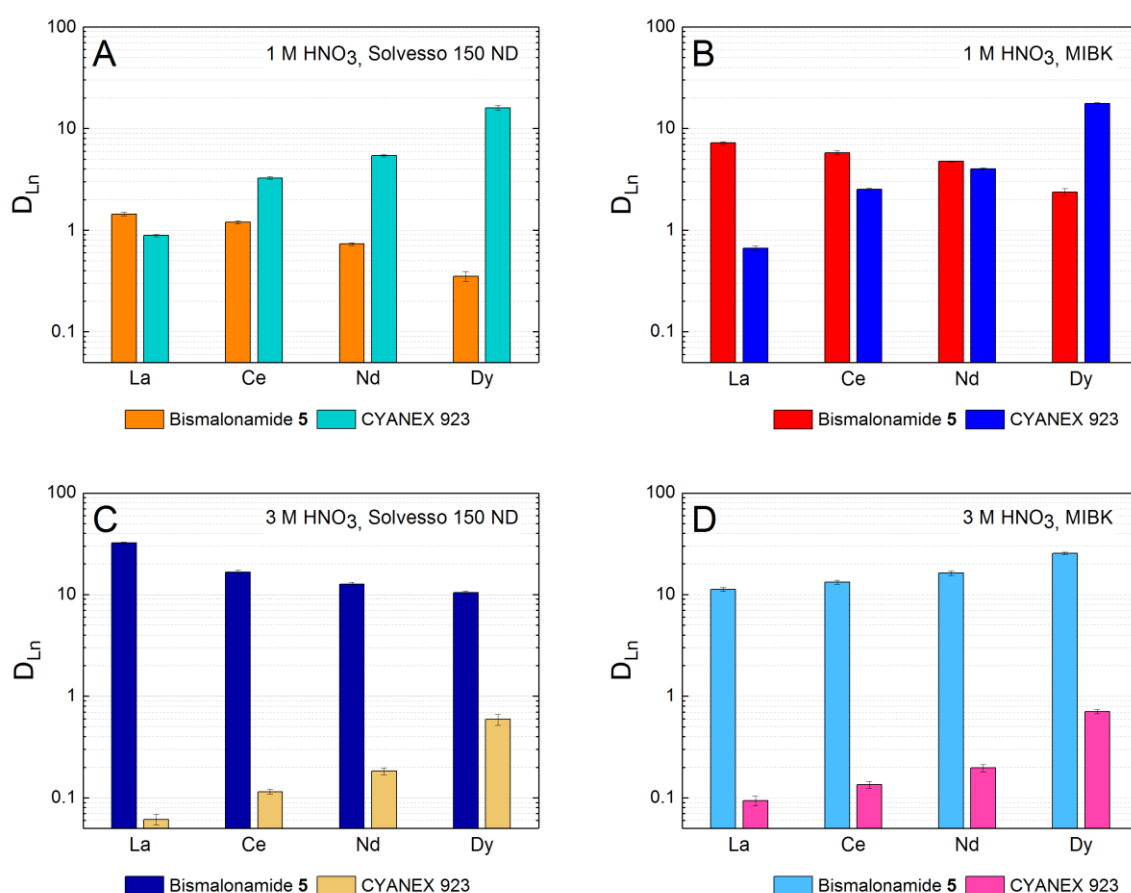
<sup>9</sup> CYANEX 923 is a mixture of four tri-*n*-alkylphosphine oxides:  $\text{R}_3\text{PO}$ ,  $\text{R}'_3\text{PO}$ ,  $\text{R}_2\text{R}'\text{PO}$  and  $\text{RR}'_2\text{PO}$ , where R and R' are the hexyl and the octyl groups, respectively. CYANEX 921 is the tri-*n*-octylphosphine oxide.

<sup>10</sup> Initially bismalonamide **5** was obtained as the liquid. It transformed into the solid with time. The organic solutions of bismalonamide **5** were prepared using bismalonamide **5** in its liquid state.

New Kankberg mining area (Sweden) [151], which are being explored as the potential secondary sources of the rare earth elements. The ratios of the lanthanides(III) were selected to match those in the deposits [151].

There was no extraction of the lanthanides(III) either with bismalonamide **5** or with CYANEX 923 when using the chloride or sulfate media in the aqueous phases. Besides that a solid third phase formed when the organic phase was the solution of bismalonamide **5** in MIBK. The common medium of the aqueous phases for the extraction of lanthanides with the solvating extractants is the nitrate one [7], though it is possible to extract trivalent f-block elements with the bidentate malonamides from the chloride medium if the aqueous phase contains a salting-out reagent (e.g. LiCl) in a high concentration [152].

In the reactions of extraction of the lanthanides(III) with bismalonamide **5** and CYANEX 923 from the nitrate media into Solvesso 150 ND or MIBK the distribution ratios of the metal ions depend on the nitric acid concentration in the aqueous phases (Fig. 44).



**Figure 44** – The distribution ratios of the lanthanides(III) in the extraction reactions with **5** and CYANEX 923. The org. phases: 0.37 M bismalonamide **5** or 0.73 M CYANEX 923 in Solvesso 150 ND (A, C) or MIBK (B, D). The aq. phases:  $(3.61 \pm 0.04)$  mM La,  $(5.20 \pm 0.04)$  mM Ce,  $(3.39 \pm 0.01)$  mM Nd,  $(0.68 \pm 0.01)$  mM Dy, 0.1 mM H<sub>3</sub>PO<sub>4</sub>, 1 M HNO<sub>3</sub> (A, B);  $(3.59 \pm 0.01)$  mM La,  $(5.14 \pm 0.03)$  mM Ce,  $(3.23 \pm 0.03)$  mM Nd,  $(0.66 \pm 0.01)$  mM Dy, 0.1 mM H<sub>3</sub>PO<sub>4</sub>, 3 M HNO<sub>3</sub> (C, D). The uncertainty bars are at  $\pm 1\sigma$ .

When the nitric acid concentration was increased from 1 M to 3 M HNO<sub>3</sub> the distribution ratios of the lanthanides(III) increased in the reactions with bismalonamide **5** and decrease in those with CYANEX 923 (Fig. 44). The ability of the malonamides, including bismalonamide **5**, to extract the lanthanides from highly acidic aqueous solutions is their advantage over the solvating organophosphorus ligands.

The diluents of the organic phases have no effect on the distribution ratios of the lanthanides(III) in the reactions with CYANEX 923 (Fig. 44). In the extraction reactions with bismalonamide **5** from the 1 M HNO<sub>3</sub> solutions the distribution ratios of the metal ions are higher when using the polar MIBK as the diluent of the organic phases (Fig. 44 A and B). In the extraction reactions with bismalonamide **5** from the 3 M HNO<sub>3</sub> solutions the order of the selectivity of the lanthanide(III) extraction with respect to their ionic radii is affected by the diluent (Fig. 44 C and D). The distribution ratios of the lanthanides in the reactions decrease in the order: La > Ce > Nd > Dy when using Solvesso 150 ND as the diluent of the organic phase (Fig. 44 C). This order is reversed in the reactions with the MIBK diluent (Fig. 44 D). In all reactions with CYANEX 923 the distribution ratios of the lanthanides increase with the decrease of their ionic radii, i.e. in the order La < Ce < Nd < Dy (Fig. 44).

### 6.6.2 Comparison of bismalonamide **5** with TBP in the extraction reactions of the f-block elements

Tri-*n*-butyl phosphate (TBP) (Fig. 43), dissolved in an inert aliphatic diluent, is used as the extractant for uranium and plutonium from nitric acid solutions in the PUREX<sup>11</sup> process, which is the ‘premier scheme for reprocessing spent nuclear reactor fuels’ [116].

The composition of the spent fuel depends on many factors (the cooling time, the enrichment of uranium, the burnup *etc.*). However its main components are the uranium, the trans-uranium elements and the fission products. According to Choppin *et al.* one metric ton of the irradiated uranium<sup>12</sup> after one year of cooling contains 14 kg of the trans-uranium elements and 63 kg of the fission products, 18.65 kg of which are yttrium and the lanthanides (in kg): Y (0.72), La (2.2), Ce (4.3), Pr (2.0), Nd (7.2), Pm (0.06), Sm (1.3), Eu (0.33), Gd (0.52), Tb – Ho (0.015) [3]. Thus these elements represent 29.6 % of the mass of the fission products.

The bismalonamide **5** was compared with TBP and *N,N,N',N'*-tetrabutylmalonamide **1** (TBMA) in the extraction reactions of the f-block elements. The aqueous phases in these reactions contained 6 M HNO<sub>3</sub> and the dissolved genuine spent nuclear fuel. Solvesso 150 ND was used as the diluent of the organic phases. The distribution ratios of the lanthanides(III) and the actinides in the extraction reactions were determined by using inductively coupled plasma–mass spectrometry (ICP-MS). They are presented in Fig. 45.

In all studied extraction reactions the distribution ratios of each of the f-block element decreased in the order of the extractants: bismalonamide **5** > TBMA **1** > TBP (Fig. 45). There was no extraction of the lanthanides(III) and yttrium(III) with TBMA (**1**) and TBP.

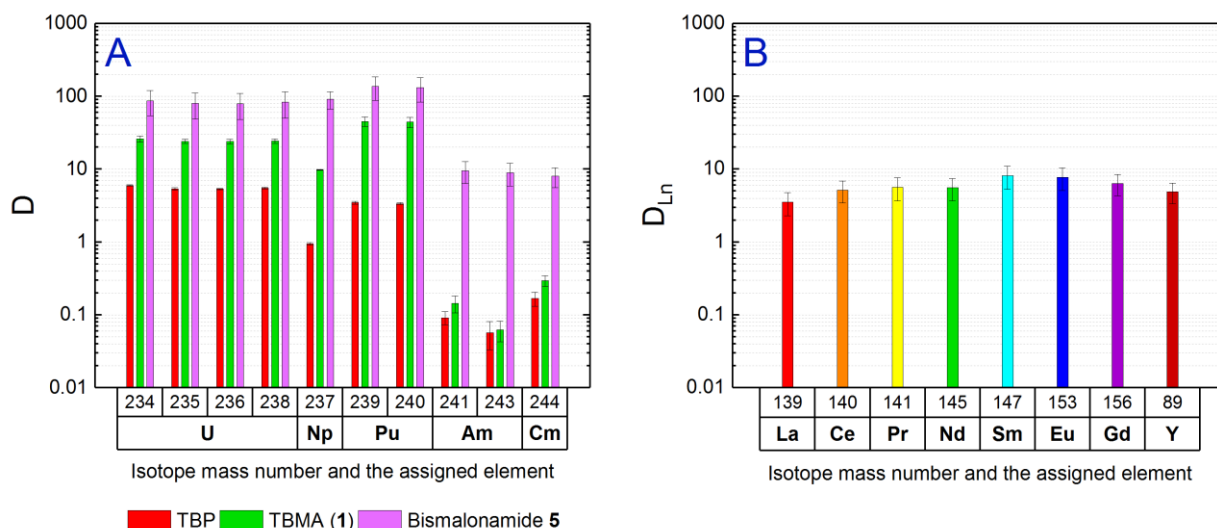
The distribution ratios of the f-block elements decrease in the following orders: Pu ≥ U ≈ Np >> Cm ≈ Am ≥ Ln (in the reactions with bismalonamide **5**); Pu > U > Np >> Cm > Am (in the reactions with TBMA); U > Pu > Np >> Cm ≥ Am (in the reactions with TBP) (Fig. 45).

In the nitrate media bismalonamide **5** is more selective for the hexa- and tetravalent f-block elements than for the trivalent ones (Fig. 45). It selectively extracts U(VI) and Th(IV) from the aqueous phases with the nitric acid concentration below two moles per liter, leaving the lanthanides(III) in the aqueous phases<sup>13</sup> (Fig. 46).

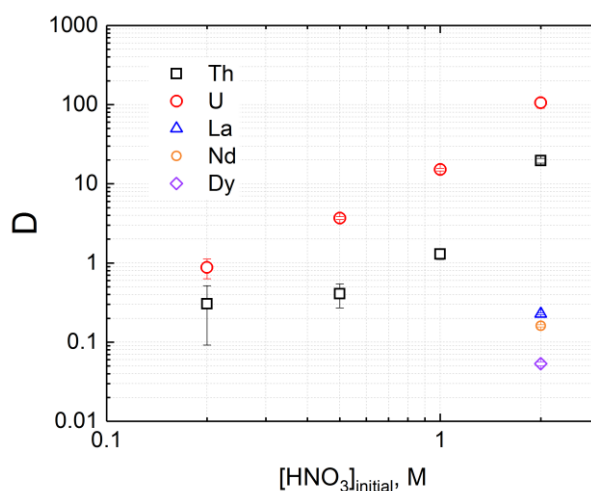
<sup>11</sup> PUREX is the acronym for ‘Plutonium Uranium Extraction’ or ‘Plutonium Uranium Reduction Extraction’.

<sup>12</sup> 3.6 % enriched UO<sub>2</sub> fuel with 60 MWd/kg U burnup in a typical BWR, where the n-flux changes yearly after fuel rearrangement.

<sup>13</sup> It was reported previously (section 6.5) that there is no extraction of the lanthanides(III) and yttrium(III) with bismalonamide **5** into Solvesso 150 ND, modified with 10 vol. % 1-decanol, from the aqueous solutions, which have the nitric acid concentrations below two moles per liter.



**Figure 45** – The distribution ratios of the 5f-block elements in the extraction reactions with bismalonamide **5**, *N,N,N',N'*-tetrabutylmalonamide **1** (TBMA) and TBP (**A**). The distribution ratios of the 4f-block elements in the extraction reactions with bismalonamide **5** (**B**). The org. phases: 0.2 M extractant in Solvesso 150 ND. The aq. phase: the dissolved genuine spent nuclear fuel (0.253(1) g/L U), 6 M HNO<sub>3</sub>. The valences of the 5f-block elements in the aq. phases were not adjusted. The uncertainty bars are at  $\pm 1\sigma$ .



**Figure 46** – The dependencies of the distribution ratios of U(VI), Th(IV) and trivalent La, Nd and Dy on an initial nitric acid concentration in the aqueous phases. The aq. phases: (0.100  $\pm$  0.005) mg/L each element – U, Th, Y, the lanthanide(III) series excluding Pm; (0.2 – 2.0) M HNO<sub>3</sub>. The org. phase: 0.18 M tetraamide **5** in Solvesso 150 ND, 10 vol. % 1-decanol. The uncertainty bars are at  $\pm 1\sigma$ .

It is not always possible to conduct selective extraction of trivalent f-block elements with conventional bidentate malonamides from nitrate media in the presence of iron(III). In the hydrometallurgical reprocessing of spent nuclear fuel iron is present in the aqueous solutions as a result of corrosion. Iron(III) and trivalent f-block elements are often co-extracted by the bidentate malonamides [36]. The selectivity of bismalonamide **5** was higher for trivalent lanthanides than for iron(III) (Table 15). The average separation factor for a lanthanide(III) – iron(III) pair in these reactions was approximately 25.

**Table 15** – The distribution ratios of the lanthanides(III) and iron(III). The aq. phase: 1.4 mM La, 1.4 mM Nd, 1.3 mM Eu, 1.2 mM Dy, 0.9 mM Fe, 1 M HNO<sub>3</sub>, 4 M NH<sub>4</sub>NO<sub>3</sub>. The org. phase: 0.18 M tetraamide **5** in nitrobenzene.

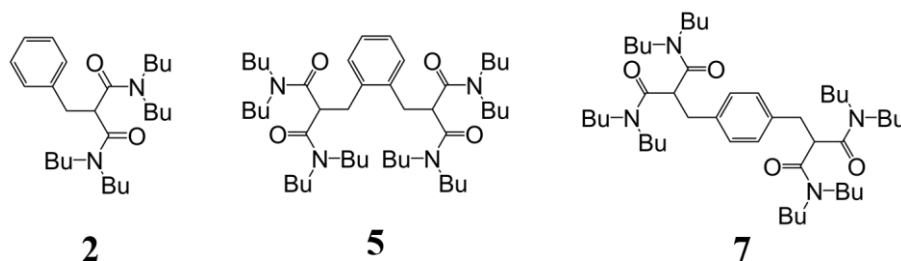
Element	Distribution ratio
La	50 ± 5
Nd	58 ± 6
Eu	49 ± 5
Dy	47 ± 5
Fe	1.7 ± 0.5

The obtained results (Fig. 45 and 46) confirmed that the bismalonamide ligands, such as **5**, potentially can be used for co-extraction of minor actinides (Am, Cm) and lanthanides from highly acidic aqueous solutions, which is the aim for the advanced reprocessing of spent nuclear fuel in the DIAMEX process [116].

### 6.7 Thermodynamics of the lanthanide(III) extraction with the bismalonamides from perchlorate media into methyl isobutyl ketone

It has been suggested by many researchers [12, 13, 37] that polydentate solvent extraction ligands could extract lanthanides(III) with higher distribution ratios than conventional extractants due to the entropic effect<sup>14</sup>. This hypothesis has not been proved by an experiment yet. The standard enthalpy changes of the europium(III) nitrate extraction reactions were compared by Ansari *et al.* for the polydentate ligand, carrying three diglycolamide groups, and conventional tri-*n*-octylphosphine oxide (TOPO) [17]. However no conclusion on the reality of the entropic effect in the reaction with this polydentate ligand can be drawn, because the structure of its ligating groups differs from that of TOPO, which was selected as the reference ligand [17].

The thermodynamic parameters of the reactions of lanthanide(III) extraction from perchlorate media into methyl isobutyl ketone (MIBK) with three structurally related amides were investigated (Fig. 47).

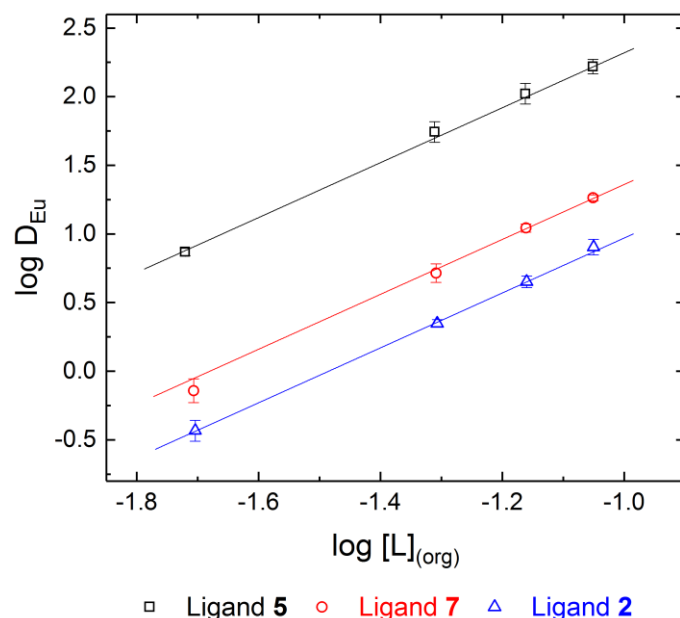


**Figure 47** – Molecular structures of the solvent extraction ligands **2**, **5** and **7**.

<sup>14</sup> By the analogy with the chelate effect in solutions, the entropic effect in the extraction reactions can be defined as the greater stability of the extracted complexes containing coordinated polydentate ligands compared with an extracted complex containing the equivalent number of the structurally analogous ligands, having lower denticities.

The related structures of these ligands allow one to pursue justified comparison of the thermodynamic parameters of the reactions of lanthanide(III) extraction. The extraction reactions were conducted in the perchlorate media to avoid the formation of multiple extracted complexes.

The empirical stoichiometric coefficients ( $n$ ) in the reactions of lanthanide(III) extraction with ligands **2** and **7** from perchlorate media into MIBK were determined by the slope analysis (Fig. 48).



**Figure 48** – The distribution ratios of Eu(III) as functions of the initial ligand concentrations in the organic phases (in the log scales) at  $T = 298$  K and  $p = 0.1$  MPa. The organic phases:  $(0.02 - 0.09)$  M of **2**, **5** or **7** in MIBK. The aqueous phases:  $0.1$  M  $\text{HClO}_4$ ,  $3$  M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb. The uncertainty bars are at  $\pm 2\sigma$ . Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa. The solid lines are the linear regressions with the slopes = 2.

The stoichiometric coefficients, calculated from the eq. (9), are listed in Table 16. These coefficients ( $n = 2$ ) are the same for the reactions with all three amide extractants.

**Table 16** – The empirical stoichiometric coefficients ( $n$ ), determined by the graphic slope analysis at  $T = 298$  K and  $p = 0.1$  MPa in the extracted complexes  $\text{Ln}(\text{ClO}_4)_3 \cdot L_{n(\text{org})}$ , formed in the reactions of the lanthanide(III) extraction with ligands **2**, **5** or **7**.<sup>a,b</sup> The organic phases:  $(0.02 - 0.09)$  M of **2**, **5** or **7** in MIBK. The aqueous phases:  $0.1$  M  $\text{HClO}_4$ ,  $3$  M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

Ligand	Stoichiometric coefficient <sup>c</sup>					
	La	Nd	Eu	Dy	Er	Yb
<b>5</b>	1.91 (0.02)	2.03 (0.03)	2.04 (0.05)	2.05 (0.05)	2.08 (0.03)	2.10 (0.03)
<b>7</b>	2.12 (0.08)	2.21 (0.10)	2.13 (0.06)	2.06 (0.06)	2.01 (0.14)	1.94 (0.21)
<b>2</b>	1.99 (0.19)	2.00 (0.13)	2.04 (0.10)	1.97 (0.10)	1.93 (0.10)	1.80 (0.11)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup>  $\text{Ln}$  is a lanthanide ion,  $L$  is a molecule of an extractant.

<sup>c</sup> The values in parentheses are the uncertainties at  $\pm 2\sigma$ .



The species  $\text{Ln}(\text{ClO}_4)_3 \cdot \text{L}_{2(\text{org})}$ , dominating in the organic phases, has the (1:2) metal-to-ligand stoichiometric ratio. The crystal structures of the lanthanide(III) complexes with the conventional bidentate malonamides, such as *N,N,N',N'*-tetraethylmalonamide, and weakly coordinating counter-ions (i.e. perrhenates [134], hexafluorophosphates [133] *etc.*) have the (1:4) metal-to-ligand ratio exclusively (with the singular exception of the (1:5) ratio in the complex of lanthanum(III) [65]). In these structures the eight-coordinate lanthanide(III) ions are surrounded by four bidentate malonamide ligands, whilst counter-ions are not coordinating to the metal ions.

The coordination of the lanthanide(III) ions with only two bidentate ligands **2** in the extracted species  $\text{Ln}(\text{ClO}_4)_3 \cdot \text{L}_{2(\text{org})}$  would create the unsaturated coordination environment for the lanthanide central atom. The vacant coordination sites must be filled in by either molecules of the diluent (methyl isobutyl ketone) or water or less likely by perchlorate anions. In the extracted complexes with the (1:2) metal-to-ligand stoichiometric ratios the isomeric ligands **5** and **7** might coordinate with lanthanide(III) ions by different modes (Fig. 23).

The coordination modes (a) and (c) (Fig. 23) were observed in the crystal structures **17** and **18**, respectively. The modes of coordination of ligands **5** and **7** with the lanthanides(III) in the extracted complexes  $\text{Ln}(\text{ClO}_4)_3 \cdot \text{L}_{2(\text{org})}$  cannot be established from the slope analysis data. However considering the fact, that two *N,N,N',N'*-tetrabutylmalonamide ligating groups are separated from each other by six carbon atoms of the *para*-xylylene rigid platform in **7**, while in **5** these are separated by only four carbon atoms of the *ortho*-xylylene platform (Fig. 35), it can be assumed that the most probable coordination modes of the ligands with lanthanides in the extracted complexes would be (a) for **7** and (c) for **5** (Fig. 23).

The enthalpy and entropy changes of the extraction reactions, being likely affected by the coordination modes of the extraction ligands, are expected to be different for the isomers **5** and **7** due to the entropic effect. The coordination mode of ligand **2**, selected as the reference extractant, can only be of the (a) type (Fig. 23). Therefore it is expected that the enthalpy and entropy changes of the lanthanide(III) extraction reactions with ligands **7** and **2** would be similar. The direct comparison of the enthalpy and entropy changes of the lanthanide(III) extraction reactions with ligands **2**, **5** and **7** is possible, since the stoichiometric coefficients in these reactions are the same .

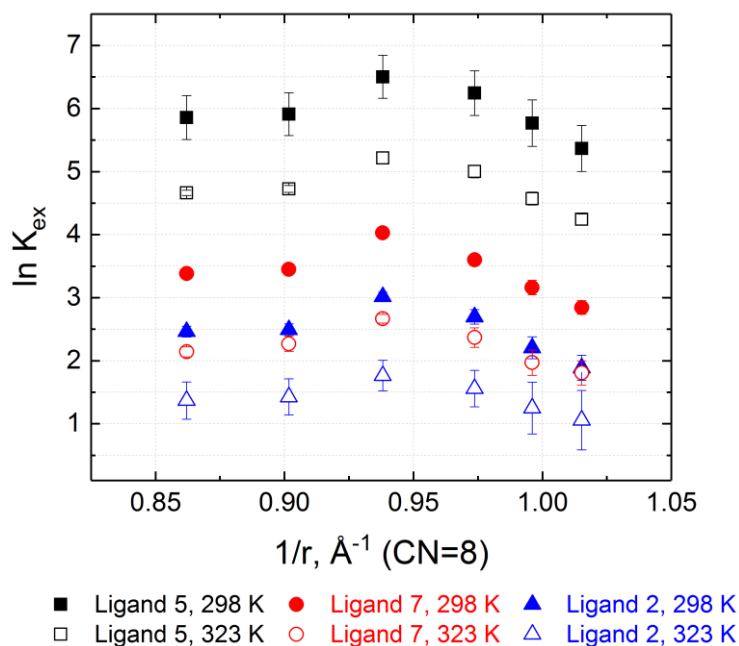
### 6.7.1 The dependencies of the apparent extraction reaction constants on temperature

It was demonstrated for some solvating ligands, e.g. trioctylphosphine oxide (TOPO), that within a narrow temperature interval the mechanism of the extraction reactions of trivalent f-block metals does not change with temperature [153]. Therefore it is reasonable to investigate the stoichiometry of a solvent extraction reaction at one temperature and expand the results into the small temperature range. In this work it was accepted that the (1:2) metal-to-ligand stoichiometry in the extracted complexes, established at  $T = 298.0$  K, is retained within the temperature range  $T = (298 - 323)$  K for all three ligands **2**, **5** and **7**.

The values of the apparent equilibrium constants  $K_{ex}$  of the lanthanide(III) extraction reactions were calculated from the eqn. (9) using the stoichiometric coefficient  $n = 2$ . These values are listed in Tables A.1 – A.3.

The dependencies of  $K_{ex}$  on the inverse lanthanide ionic radii are non-monotonic (Fig. 49). The similar dependencies have been reported for the lanthanide(III) extraction reactions from nitrate media with the solvating extractants, for instance tri-*n*-butyl phosphate (TBP) [8, 9, 154] and carbamoylmethylphosphine oxides (CMPO) [155], and explained by the increase in hydration energy

of the lanthanide(III) ions with the decrease of the ionic radii, and the ability of the solvating ligands to dehydrate the lanthanide(III) ions during extraction [155].



**Figure 49** – The semi-log plots of the apparent equilibrium constants  $K_{ex}$  of the lanthanide(III) extraction reactions with ligands 2, 5 and 7 at  $p = 0.1$  MPa and  $T = 298$  K (the closed symbols) or  $T = 323$  K (the open symbols), as functions of the inverse lanthanide(III) ionic radii. The organic phases: 0.05 M amides 2, 5 or 7 in MIBK. The aqueous phases: 0.1 M  $\text{HClO}_4$ , 3 M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb. The error bars denote the standard uncertainties. The ionic radii for the eight-coordinate lanthanides(III) are taken from Shannon [132].

The standard Gibbs energy changes  $\Delta_r G^\circ$  of the extraction reactions (Table 17) were calculated from the eqn. (10).

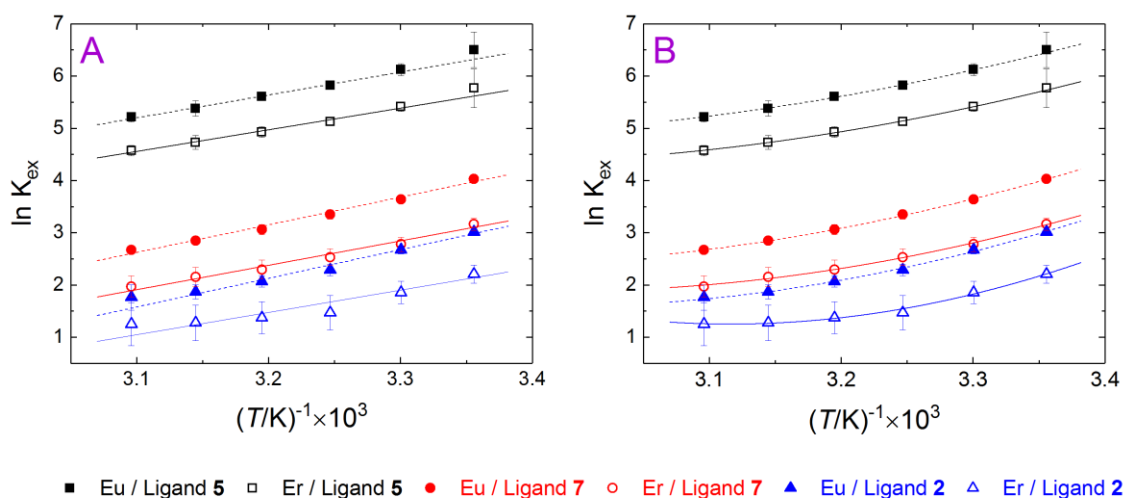
**Table 17** – The standard molar Gibbs energy changes ( $\Delta_r G^\circ_{298}$ ) of the reactions of the lanthanide(III) extraction with ligands 2, 5 and 7 at  $T = 298$  K and  $p = 0.1$  MPa, calculated from eqn. (10).<sup>a,b</sup> The organic phases: 0.05 M amides 2, 5 or 7 in MIBK. The aqueous phases: 0.1 M  $\text{HClO}_4$ , 3 M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

lanthanide(III)	$\Delta_r G^\circ_{298}, \text{kJ} \cdot \text{mol}^{-1}$		
	Ligand 5	Ligand 7	Ligand 2
La	-14.5 (0.7)	-8.4 (0.1)	-6.1 (0.2)
Nd	-14.6 (0.7)	-8.5 (0.1)	-6.2 (0.2)
Eu	-16.1 (0.7)	-10.0 (0.1)	-7.5 (0.1)
Dy	-15.5 (0.7)	-8.9 (0.2)	-6.7 (0.2)
Er	-14.3 (0.7)	-7.8 (0.2)	-5.5 (0.3)
Yb	-13.3 (0.7)	-7.0 (0.2)	-4.7 (0.4)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup> The values in parentheses are the uncertainties at  $\pm 2\sigma$ .

The equations (11) and (15) were used to test the hypothesis, that the standard entropy and enthalpy changes of the reactions of the lanthanide(III) extraction with ligands **2**, **5** and **7** from perchlorate media into MIBK depend on temperature.



**Figure 50** – The semi-log plots of the apparent equilibrium constants  $K_{ex}$  of the  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$  extraction reactions as functions of the reciprocal of absolute temperature at  $p = 0.1$  MPa. The organic phases: 0.05 M amide **2**, **5** or **7** in MIBK. The aqueous phases: 0.1 M  $\text{HClO}_4$ , 3 M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb. The solid and dash lines are the linear regressions (A), calculated from eqn. (10), and the non-linear regressions (B), calculated from eqn. (15). The error bars denote the standard uncertainties. Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

The non-linear eqn. (15) fit the experimental data better than the linear eqn. (10) (Fig. 4.7.1.2). This fact implies that the effect of temperature on the standard entropy and enthalpy changes of the lanthanide(III) extraction reactions cannot be neglected. Further the standard entropy and enthalpy changes of the extraction reactions are considered as being temperature dependent.

The differences in the standard molar heat capacities of the reactants and the products ( $\Delta C_p^\circ$ ) in the reactions of the lanthanide(III) extraction with **2**, **5** and **7** were calculated from eqn. (15) and listed in Table 18. The values of  $\Delta C_p^\circ$  are all positive (Table 18).

The values of  $\Delta C_p^\circ$  increase with the decrease of the lanthanide(III) ionic radii in the extraction reactions with **2** (Table 18). In the reactions with ligand **5** the values of  $\Delta C_p^\circ$  are rather independent of the lanthanide(III) ionic radii (Table 18). In the reactions with ligand **7** the values of  $\Delta C_p^\circ$  are also rather independent of the lanthanide(III) ionic radii but increase in the reaction of Yb extraction (Table 18). These observations seem to be reasonable for the following reasons. Spedding *et al.* discovered that at 25° C the apparent molal heat capacities of aqueous rare earth perchlorate solutions increase from light to heavy metal ions across the lanthanide series in accordance with an increase of the charge densities at the surface of the ions [156]. Similarly the size of the extracted lanthanide(III) complex with ligand **2** is expected to be smaller than those of the complexes with ligands **5** and **7**, and consequently the charge density at the surface of this complex should be higher.

**Table 18** – The differences in the standard molar heat capacities of the reactants and the products ( $\Delta C_p^\circ$ ) in the reactions of the lanthanide(III) extraction with ligands **2**, **5** and **7** at  $T = (298 - 323)$  K and  $p = 0.1$  MPa, calculated from eq. (15).<sup>a,b</sup> The organic phases: 0.05 M amide **2**, **5** or **7** in MIBK. The aqueous phases: 0.1 M HClO<sub>4</sub>, 3 M NaClO<sub>4</sub>,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

Lanthanide(III)	Radius <sup>c</sup> , Å	$\Delta C_p^\circ / (\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$		
		Ligand <b>5</b>	Ligand <b>7</b>	Ligand <b>2</b>
La	1.160	1.23 (0.16)	1.23 (0.16)	1.51 (0.85)
Nd	1.109	0.99 (0.11)	1.42 (0.32)	1.93 (0.47)
Eu	1.066	1.03 (0.27)	1.33 (0.13)	1.58 (0.45)
Dy	1.027	1.13 (0.20)	1.07 (0.08)	2.29 (0.39)
Er	1.004	1.13 (0.22)	1.53 (0.31)	2.88 (0.49)
Yb	0.985	1.14 (0.22)	1.88 (0.19)	3.43 (0.69)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup> The values in parentheses are the standard uncertainties.

<sup>c</sup> The ionic radii for the eight-coordinate lanthanide(III) ions are taken from Shannon [132].

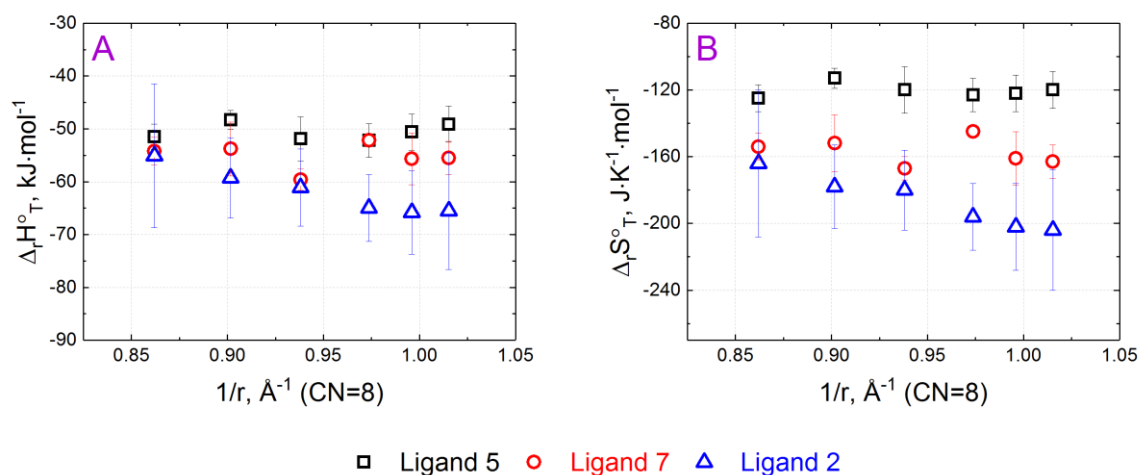
If the extracted complexes with ligand **5** are coordinatively saturated (i.e. assuming that both molecules of **5** are tetradentate in the complex) the  $\Delta C_p^\circ$  should be barely dependent on the ionic radii of the metal ions because of the ligand shielding of the lanthanide(III) inner sphere from interactions with organic diluent molecules or perchlorate counter-ions.

### 6.7.2 The standard molar enthalpy and entropy changes of the lanthanide(III) extraction reactions

The standard molar entropy and enthalpy changes of the lanthanide(III) extraction reactions with ligands **2**, **5** and **7**, calculated from eqn. (15), were analyzed as functions of the inverse lanthanide ionic radii (Fig. 51).

The standard molar enthalpy changes of the reactions of lanthanide(III) extraction with ligands **5** and **7** are exothermic at  $T = 298$  (Table 19) and rather independent of the lanthanide(III) ionic radii at  $T = 298$  K (Fig. 51 A). The standard molar enthalpy changes in the reactions of lanthanide(III) extraction with ligand **2** are also exothermic at  $T = (298 - 323)$  K (Table 19), except for the reactions of extraction of the heavy lanthanides erbium and ytterbium at  $T = 323$  K with the endothermic  $\Delta_r H^\circ_T$ , and depend on the lanthanide(III) ionic radii (Fig. 51), since the corresponding differences in the standard molar heat capacities of the reactants and the products ( $\Delta C_p^\circ$ ) depend on the ionic radii (Table 18 and eqn. 12). The exothermic standard molar enthalpy changes in the reactions of lanthanide(III) extraction with ligands **2**, **5** and **7** indicate that the energy of bond formation between a lanthanide ion and a ligand in the organic phases exceeds the energy of the metal ion dehydration.

All studied reactions of lanthanide(III) extraction with ligands **2**, **5** and **7** were found to be enthalpy-driven at  $T = (298 - 323)$  K (Tables 17 and 18).



**Figure 51** – The standard molar enthalpy (A) and entropy (B) changes of the reactions of lanthanide(III) extraction with ligands 2, 5 and 7, calculated from eqn. (15) at  $T = 298\text{ K}$  and  $p = 0.1\text{ MPa}$ , as functions of the inverse lanthanide(III) ionic radii. The organic phases: 0.05 M amides 2, 5 or 7 in MIBK. The aqueous phases: 0.1 M  $\text{HClO}_4$ , 3 M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}\text{ M}$  of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb. The error bars are the standard uncertainties. Standard uncertainties  $u$  are  $u(T) = 0.1\text{ K}$  and  $u(p) = 0.005\text{ MPa}$ . The ionic radii for the eight-coordinate lanthanide(III) ions are taken from Shannon [39].

It is important to notice that in the reactions of lanthanide(III) extraction with ligands 2, 5 and 7 at  $T = 298\text{ K}$  the least exothermic standard molar enthalpy changes were observed for ligand 5 (Fig. 51 A) despite the fact, that the largest constants of the lanthanide(III) extraction were obtained in the reactions with this ligand (Fig. 49).

**Table 19** – The standard molar enthalpy ( $\Delta_r H^\circ_{298}$ ) and entropy ( $\Delta_r S^\circ_{298}$ ) changes of the reactions of the lanthanide(III) extraction with ligands 2, 5 and 7 at  $T = 298\text{ K}$  and  $p = 0.1\text{ MPa}$ , calculated from eqn. (15).<sup>a,b</sup> The organic phases: 0.05 M amide 2, 5 or 7 in MIBK. The aqueous phases: 0.1 M  $\text{HClO}_4$ , 3 M  $\text{NaClO}_4$ ,  $(0.100 \pm 0.002) \cdot 10^{-3}\text{ M}$  of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

Ln(III)	Ligand 5		Ligand 7		Ligand 2	
	$\Delta_r H^\circ_{298}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_r S^\circ_{298}$ , $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_r H^\circ_{298}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_r S^\circ_{298}$ , $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta_r H^\circ_{298}$ , $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_r S^\circ_{298}$ , $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
La	-51.5 (2.4)	-124.7 (7.9)	-54.2 (2.6)	-153.7 (8.5)	-55.1 (13.6)	-164.2 (44.4)
Nd	-48.3 (1.8)	-113.2 (5.8)	-53.8 (5.1)	-151.9 (16.7)	-59.3 (7.6)	-178.1 (24.8)
Eu	-51.9 (4.2)	-120.5 (13.9)	-59.6 (2.0)	-166.6 (6.7)	-61.1 (7.3)	-179.8 (23.8)
Dy	-52.2 (3.2)	-123.4 (10.3)	-52.2 (1.2)	-145.1 (4.0)	-65.0 (6.3)	-195.7 (20.4)
Er	-50.6 (3.4)	-122.1 (11.1)	-55.7 (4.9)	-160.6 (15.9)	-65.8 (7.9)	-202.4 (25.7)
Yb	-49.1 (3.4)	-120.4 (11.2)	-55.5 (3.1)	-162.8 (10.1)	-65.5 (11.1)	-204.2 (36.1)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1\text{ K}$  and  $u(p) = 0.005\text{ MPa}$ .

<sup>b</sup> The values in parentheses are the uncertainties at  $\pm 2\sigma$ .

This observation can be explained by the steric hindrance effect of the amide groups of ligand **5**, which decreases the absolute values of  $\Delta_r H^\circ_T$  and, consequently,  $\Delta_r G^\circ_T$  (eqn. 14) and  $\ln K_{ex}$  (eqn. 10). It is reasonable to assume that this effect takes place in the extraction reactions with all three structurally related malonamide ligands **2**, **5** and **7**. However the effect should be stronger in the reactions with **5**, than with **7** and **2**, if these ligands have different coordination with the lanthanides(III) (Fig. 23). Since the experimental data indicate that the steric hindrance effect is stronger in the reactions with ligand **5** (Fig. 51 A), it can be concluded that in the extracted complexes this ligand is likely bonded to a lanthanide(III) ion by all four carbonyl oxygen atoms (Fig. 23 c), while ligands **7** and **2** coordinate with the central atoms with only two oxygen atoms (Fig. 23 a).

The standard molar entropy changes of the reactions of lanthanide(III) extraction with ligands **5** and **7** have negative values at  $T = (298 - 323)$  K (Table 19) and independent of the lanthanide(III) ionic radii at  $T = 298$  K (Fig. 51 B). The standard molar entropy changes in the reactions of lanthanide(III) extraction with ligand **2** also have negative values at  $T = (298 - 323)$  K (Table 19), except for the reactions of extraction of the heavy lanthanides erbium at  $T = 323$  K and ytterbium at  $T = (318 \text{ and } 323)$  K, having positive  $\Delta_r S^\circ_T$ , and depend on the lanthanide(III) ionic radii (Fig. 51 B), since the corresponding differences in the standard molar heat capacities of the reactants and the products ( $\Delta C^\circ_p$ ) depend on the ionic radii (Table 18 and eqn. 13).

The standard molar entropy changes of the reactions ( $\Delta_r S^\circ_T$ ), having negative values, decrease the absolute values of the standard Gibbs energy change of a reaction ( $\Delta_r G^\circ_T$ ) (eqn. 14) (considering that  $\Delta_r H^\circ_T$  are negative), which in turn decreases the corresponding apparent equilibrium constant ( $K_{ex}$ ) of the lanthanide(III) extraction reaction (eqn. 10). In the reactions of lanthanide(III) extraction with ligands **2**, **5** and **7** at  $T = 298$  K the standard molar entropy changes with the least negative values were observed for ligand **5** (Fig. 51 B). This observation is consistent with the fact, that the largest apparent equilibrium constants ( $K_{ex}$ ) of the lanthanide(III) extraction reactions were obtained with ligand **5** (Fig. 49). It is assumed that the differences in the standard molar entropy changes of the reactions with ligands **2**, **5** and **7** reflect the differences in the coordination of these ligands with the lanthanides(III).

The comparison of the standard molar entropy and enthalpy changes of the reactions of lanthanide(III) extraction from perchlorate media into MIBK with the structurally related ligands **5**, **7** and **2** allowed one to conclude, that the distribution ratios of the lanthanide(III) ions were higher in the reactions with ligand **5**, than with ligands **7** and **2**, due to the entropic effect.

## Summary and conclusions

Advanced hydrometallurgical recycling of electric and electronic waste streams, containing rare earth elements, and used nuclear fuel requires efficient and environmentally friendly solvent extraction ligands for recovery of lanthanide ions.

This thesis was aiming at design, synthesis and evaluation of novel polydentate amide extractants for lanthanides(III). It was reasoned early on that polydentate amides could extract lanthanides(III) with higher distribution ratios than conventional amides due to the entropic effect. The molecules of the synthesized polydentate amide extractants **3** – **8** contain malonamide ligating groups. The malonamide sub-units were selected since malonamides are known to be able to extract lanthanides from nitric acid solutions, to be stable against nitric acid, to be possible to form from relatively cheap reagents and to adhere to the ‘CHON’ principle. The ‘CHON’ principle is the requirement that the substance should be capable of being incinerated without the formation of ash and acid gases (other than the nitrogen oxides). The comparison of the distribution ratios of europium(III) in the extraction reactions with the bidentate (**1**), tridentate (**3** and **4**) and tetradentate (**5**) amide ligands from nitrate media into nitrobenzene or 1,2-dichlorobenzene indicated, that there is no simple relationship between the denticity of the ligand and the distribution ratios of Eu(III), which were decreasing in the order: tetradentate amide (**5**) >> bidentate amide (**1**) > tridentate amides (**3** and **4**) in nitrobenzene; tetradentate amide (**5**) >> bidentate amide (**1**)  $\approx$  tridentate amides (**3** and **4**) in 1,2-dichlorobenzene. It was assumed that the highest distribution ratios of Eu(III), obtained in the reactions with the tetradentate amide **5**, could result from the tetradentate coordination of this ligand with the metal ion.

Slope analysis revealed that in the extraction reactions the tetradentate amide **5** forms multiple complexes with lanthanides, which have the following stoichiometric ratios of a metal and the extractant: (1:1) and (1:2) (nitrate media / nitrobenzene); (1:2), (1:3) and (1:4) (nitrate media / kerosene); (1:2) (perchlorate media / MIBK). The formation of multiple complexes of lanthanides(III) with the tetradentate amide **8**, which is the homologue of **5**, in acetonitrile solutions was confirmed both in solution and in the solid state. The observations in solution state were made with electrospray ionization – mass spectroscopy, while in the solid state four crystal structures of the amide **8** (L) with neodymium(III) and cerium(III) ions  $[\text{Nd}_2(\text{NO}_3)_6\text{L}_2] \cdot (\text{CH}_3\text{CN})_3$  (**15**),  $[\text{Nd}_2(\text{NO}_3)_4\text{L}_2] \cdot [\text{Nd}(\text{NO}_3)_3] \cdot (\text{CH}_3\text{CN})_{1.5}$  (**16**),  $\text{Ce}(\text{NO}_3)_3\text{L}_2$  (**17**) and  $[\text{NdL}_2] \cdot (\text{ClO}_4)_3 \cdot \text{C}_2\text{H}_5\text{OH}$  (**18**) were observed with single-crystal X-ray diffraction. The metal-to-ligand stoichiometric ratios in these solid state structures were either (2:2) in **15** and **16** or (1:2) in **17** and **18**. The structures **15** and **16** contain the dimers. The amide **8** is bidentate in the structure **17** and tetradentate in **18**.

It was demonstrated that the tetradentate amide **5**, in contrast to the organophosphorus TBP and CYANEX 923, extracts trivalent lanthanide ions from aqueous solutions with high nitric acid concentrations. The nature of the extracted species depends on a diluent of an organic phase. The non-acidic extracted species  $L_x \cdot M(\text{NO}_3)_{3(\text{org})}$  were observed in the reactions of extraction into polar nitrobenzene. The extracted species  $L_x \cdot M(\text{NO}_3)_{(3+y)} \cdot H_{y(\text{org})}$ , containing protons of nitric acid ( $\text{H}^+$ ), were found in the organic phases with the non-polar kerosene diluent Solvesso 150 ND. The distribution ratios of lanthanides were also affected by the polarity of the diluents of the organic phases, being the highest in nitrobenzene.

The distribution ratios of lanthanides(III) in the extraction reactions with the tetradentate amides depend on the structure of these ligands. The tetradentate amides **5** and **8** are composed of two malonamide ligating groups, attached to an ortho-xylylene platform through carbon atoms. The difference in the molecular structures of **5** and **8** is in the length of the alkyl groups attached to the amide nitrogens, being

*n*-butyl ( $n\text{-C}_4\text{H}_9$ ) in **5** and ethyl ( $\text{C}_2\text{H}_5$ ) in **8**. The distribution ratios of the lanthanides(III) and yttrium(III) were higher in the extraction reactions with **8** than with **5**, which is explained by the greater steric hindrance effect of longer *n*-butyl substituents in **5**. Three structural isomers **5**, **6** and **7**, the molecules of which contain two *N,N,N',N'*-tetrabutylmalonamide ligating groups, separated from each other by four, five and six carbon atoms of the isomeric *ortho*-, *meta*- and *para*-xylylene platforms, respectively, were compared in the extraction reactions of lanthanide(III) ions. The highest distribution ratios of these ions were obtained in the reactions with **5**, which was rationalized by the tetradentate coordination mode of **5** with lanthanide(III) ions, similar to the one observed in the crystal structure **18**. This coordination mode is possible due to the shorter distance between two ligating groups in a molecule of **5** compared to the distances in the molecules of its structural isomers **6** and **7**.

The tetradentate coordination mode may promote favorable entropy changes in the extraction reactions of lanthanides(III) with the tetradentate amide **5**. The studies of the reactions of lanthanide(III) extraction from perchlorate media into methyl isobutyl ketone with the structurally related malonamides **2**, **5** and **6** demonstrated that all these reactions are enthalpy-driven. However the least negative standard molar entropy changes of the reactions were observed for the tetradentate amide **5**. It allows one to conclude, that the distribution ratios of the lanthanide(III) ions were the highest in the reactions with **5** due to the entropic effect.

The combination of solvent extraction, single-crystal X-ray diffraction and electrospray ionization – mass spectrometry provided us with better understanding of the coordination chemistry of these extraction ligands with the lanthanides.



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## Supplementary data

CCDC 1541623 (for **15**), 1555415 (for **16**), 1541624 (for **17**) and 1541625 (for **18**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

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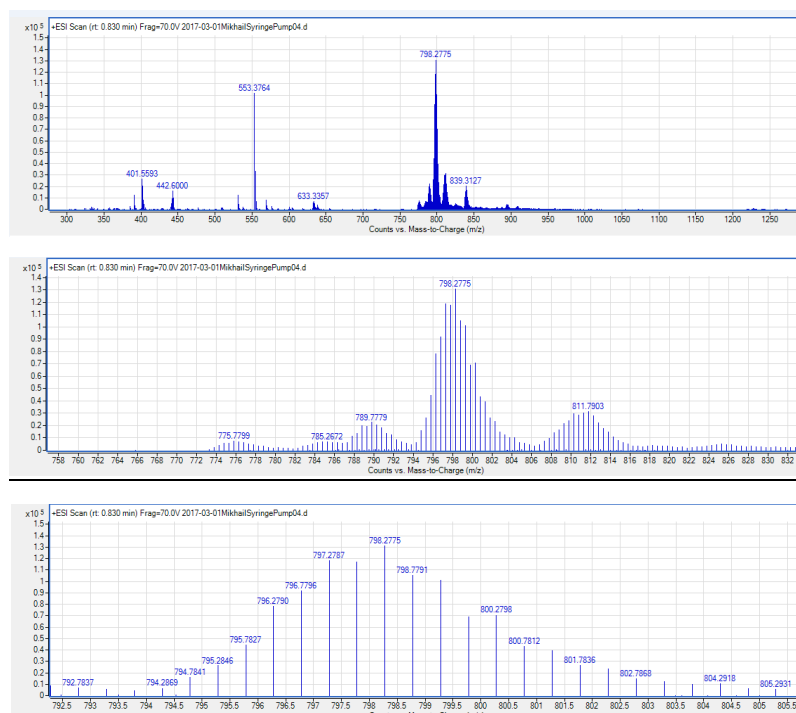
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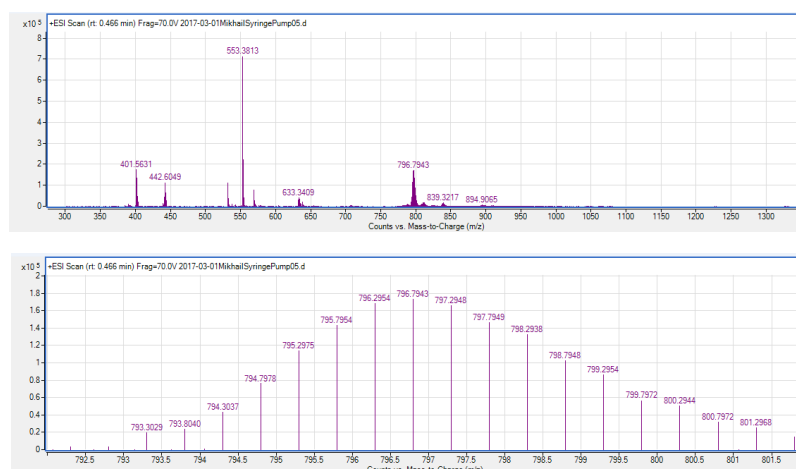
## APPENDIX

### List of abbreviations

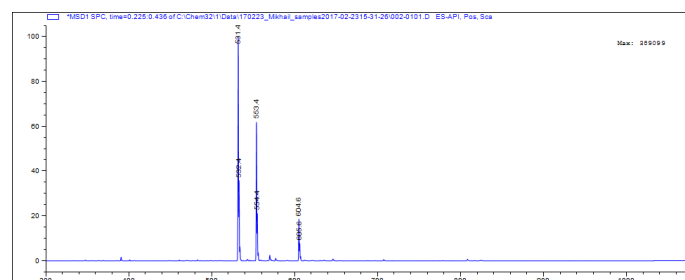
TBP	tri- <i>n</i> -butyl phosphate
TOPO	tri- <i>n</i> -octylphosphine oxide
DMDBTDMMA	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dibutyl-2-tetradecylmalonamide
DMDOHEMA	<i>N,N'</i> -dimethyl- <i>N,N'</i> -dioctyl-2-hexylethoxymalonamide
THMA	<i>N,N,N',N'</i> -tetrahexylmalonamide
MTHMA	<i>N,N,N',N'</i> -tetrahexyl-2-methylmalonamide
DMTHMA	<i>N,N,N',N'</i> -tetrahexyl-2,2-dimethylmalonamide
TMMA	<i>N,N,N',N'</i> -tetramethylmalonamide
DMBMA	2,7-dimethylhexahydro-2,7-naphthyridine-1,8(2H,5H)-dione
TEMA	<i>N,N,N',N'</i> -tetraethylmalonamide
TEEEMA	2-(2-ethoxyethyl)- <i>N,N,N',N'</i> -tetraethylmalonamide
TBMA	<i>N,N,N',N'</i> -tetrabutylmalonamide
DMDCHMA	<i>N,N'</i> -dicyclohexyl- <i>N,N'</i> -dimethylmalonamide
DMDPEEMA	2-(2-ethoxyethyl)- <i>N,N'</i> -dimethyl- <i>N,N'</i> -diphenylmalonamide
DMDPBMA	2-butyl- <i>N,N'</i> -dimethyl- <i>N,N'</i> -diphenylmalonamide
Br-TEMA	2-bromo- <i>N,N,N',N'</i> -tetraethylmalonamide
DMSO	dimethyl sulfoxide
CMPO	carbamoylmethylphosphine oxide
TRPO	trialkyl phosphine oxide
NMR	nuclear magnetic resonance
IR	infra-red
LSC	liquid scintillation counter
XRD	X-ray diffraction
rpm	revolutions per minute
b.p.	boiling point



**Fig. A1** – Positive high-resolution ESI-mass spectrum of the solution of  $\text{Nd}(\text{NO}_3)_3$  and bismalonamide **8** (L) with the 1:1 metal-to-ligand molar ratio (top image) and its expansions at  $m/z = (758 - 832)$  and  $(793 - 805)$  (bottom images). The spectrum was recorded in acetonitrile.



**Fig. A2** – Positive high-resolution ESI-mass spectrum of the solution of  $\text{Nd}(\text{NO}_3)_3$  and bismalonamide **8** (L) with the 1:2 metal-to-ligand molar ratio (top image) and its expansion at  $m/z = (793 - 801)$  (bottom image). The spectrum was recorded in acetonitrile.



**Fig. A3** – Positive ESI-mass spectrum of the bismalonamide **8** (L) solution in acetonitrile.

**Table A.1.** The natural logarithms of the apparent equilibrium constants ( $K_{ex}$ ) of the lanthanide(III) extraction reactions with ligand **5** at  $T = (298 - 323)$  K and  $p = 0.1$  MPa, calculated from eq. (4.3.1.1.2).<sup>a,b</sup> The organic phases: 0.05 M of ligand **5** in MIBK. The aqueous phases: 0.1 M HClO<sub>4</sub>, 3 M NaClO<sub>4</sub>,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

$T/K$	$\ln K_{ex}$					
	La	Nd	Eu	Dy	Er	Yb
298	5.86 (0.14)	5.91 (0.14)	6.50 (0.14)	6.25 (0.14)	5.77 (0.15)	5.37 (0.15)
303	5.49 (0.03)	5.55 (0.03)	6.12 (0.05)	5.88 (0.04)	5.41 (0.03)	5.04 (0.04)
308	5.21 (0.02)	5.29 (0.02)	5.82 (0.03)	5.58 (0.04)	5.13 (0.03)	4.76 (0.03)
313	4.99 (0.02)	5.07 (0.03)	5.61 (0.03)	5.37 (0.04)	4.93 (0.04)	4.58 (0.04)
318	4.83 (0.04)	4.88 (0.05)	5.38 (0.06)	5.16 (0.06)	4.73 (0.05)	4.38 (0.05)
323	4.66 (0.02)	4.73 (0.02)	5.22 (0.04)	5.00 (0.04)	4.57 (0.04)	4.24 (0.04)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup> The values in parentheses are the standard uncertainties.

**Table A.2.** The natural logarithms of the apparent equilibrium constants ( $K_{ex}$ ) of the lanthanide(III) extraction reactions with ligand **7** at  $T = (298 - 323)$  K and  $p = 0.1$  MPa, calculated from eq. (4.3.1.1.2).<sup>a,b</sup> The organic phases: 0.05 M of ligand **7** in MIBK. The aqueous phases: 0.1 M HClO<sub>4</sub>, 3 M NaClO<sub>4</sub>,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

$T/K$	$\ln K_{ex}$					
	La	Nd	Eu	Dy	Er	Yb
298	3.39 (0.02)	3.45 (0.02)	4.03 (0.02)	3.60 (0.04)	3.16 (0.05)	2.84 (0.04)
303	3.03 (0.03)	3.07 (0.04)	3.64 (0.02)	3.27 (0.04)	2.78 (0.05)	2.48 (0.06)
308	2.76 (0.04)	2.82 (0.04)	3.35 (0.03)	2.98 (0.05)	2.53 (0.06)	2.24 (0.06)
313	2.50 (0.03)	2.62 (0.04)	3.06 (0.04)	2.74 (0.06)	2.30 (0.07)	2.04 (0.08)
318	2.32 (0.02)	2.45 (0.04)	2.84 (0.03)	2.55 (0.06)	2.15 (0.08)	1.90 (0.07)
323	2.14 (0.03)	2.27 (0.05)	2.67 (0.03)	2.37 (0.06)	1.97 (0.08)	1.81 (0.08)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup> The values in parentheses are the standard uncertainties.

**Table A.3.** The natural logarithms of the apparent equilibrium constants ( $K_{ex}$ ) of the lanthanide(III) extraction reactions with ligand **2** at  $T = (298 - 323)$  K and  $p = 0.1$  MPa, calculated from eq. (4.3.1.1.2).<sup>a,b</sup> The organic phases: 0.05 M of ligand **2** in MIBK. The aqueous phases: 0.1 M HClO<sub>4</sub>, 3 M NaClO<sub>4</sub>,  $(0.100 \pm 0.002) \cdot 10^{-3}$  M of each lanthanide(III): La, Nd, Eu, Dy, Er, Yb.

$T/K$	$\ln K_{ex}$					
	La	Nd	Eu	Dy	Er	Yb
298	2.46 (0.03)	2.49 (0.04)	3.02 (0.03)	2.70 (0.05)	2.21 (0.07)	1.89 (0.08)
303	2.19 (0.03)	2.17 (0.04)	2.68 (0.03)	2.34 (0.05)	1.86 (0.09)	1.52 (0.10)
308	1.78 (0.06)	1.80 (0.08)	2.29 (0.05)	1.95 (0.10)	1.47 (0.13)	1.19 (0.13)
313	1.57 (0.05)	1.62 (0.06)	2.07 (0.04)	1.77 (0.08)	1.37 (0.12)	1.11 (0.16)
318	1.47 (0.03)	1.47 (0.07)	1.87 (0.06)	1.63 (0.10)	1.27 (0.14)	1.15 (0.13)
323	1.37 (0.12)	1.43 (0.12)	1.76 (0.10)	1.56 (0.12)	1.25 (0.17)	1.06 (0.19)

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(p) = 0.005$  MPa.

<sup>b</sup> The values in parentheses are the standard uncertainties.